ABSTRACT

EDWARD M. DIESER. Biofiltration of Ammonia in Air.
(Under the direction of Michael D. Aitken, Ph.D.)

Ammonia emissions from intensive livestock operations are a significant source of reactive atmospheric nitrogen. The elevated levels of ammonia cause adverse environmental and occupational health effects. Recent studies link the associated odors with symptoms common to communities neighboring these facilities. Therefore, the development of technologies to remove odor-causing emissions will be important to public acceptance of large livestock operations. A laboratory-scale biotrickling filter was designed and operated to remove ammonia from an artificially contaminated air steam. The biofilter was constructed as two 0.5 meter columns in series, each packed with an expanded clay medium (Infilco-Degremont Biolite^{TM}) and inoculated with an enriched nitrifying seed culture. The study, conducted over six weeks of continuous operation, used three sets of operational conditions. In Periods 1 and 2 an empty bed contact time (EBCT) of 28 seconds was maintained for nitrogen loading rates of 0.25 and 0.5 kg N/m^3 d, respectively. In Period 3 the higher loading rate was sustained but at an EBCT of 14 seconds. The ammonia removal was greater than 99% for all three operating conditions. Virtually all of the ammonia was converted to nitrate in the biofilter. Headloss across the media bed did not increase during any operating conditions and suspended solids in the liquid effluent remained constant at 1 mg/L, suggesting that biomass accumulation was not a problem over the six week experimental period. The results suggest that biotrickling filtration using an expanded clay medium is a viable option for the treatment of air contaminated with ammonia at high concentrations and loading rates.

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To Avril,
for her love and encouragement.

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1. INTRODUCTION

The atmosphere is universally accepted as an intrinsic part of the nutrient lifecycle of the earth's ecosystem. While the global interaction of this system is apparent, the success of local ecosystems is based in part on the nutrient balance within individual watersheds. Numerous studies demonstrate that the synergistic effects of the intensive livestock industry compound the imbalance in North Carolina. Ninety-five percent of the nutrient nitrogen (N) in the Neuse River Basin is imported from outside the basin in the form of feed by livestock operations (Hunt, 1999). Estimates of subsequent nitrogen transport through ammonia (NH_3) volatilization from swine waste storage and disposal using lagoons and sprayfields range from 60 to 80 percent (Hammond, 1994; Hunt, 1999). Studies suggest that hog operations deposit more nitrogen pollution into North Carolina estuaries through the air alone than all other municipal treatment plants and industrial factories combined (Hog Watch, 1998). In addition to ammonia, the open-air anaerobic lagoons release methane, nitrous oxide and other greenhouse gases contributing to low level ozone formation (Hog Watch, 1998; Cole et al, 1999; North Carolina Department of Environment and Natural Resources [DENR], 1999c). These large livestock operations generate more nutrients than the local ecosystem can adequately absorb. The imbalance often leads to over-enrichment of surface water and eutrophication, depleting the water of dissolved oxygen. The low dissolved oxygen levels in turn disrupt the aquatic environment, catastrophically evident in fish kills.

Environmental health does not stand alone is this dilemma. Numerous studies link agricultural emissions to adverse human health effects in workers and neighboring communities. Particulate and gaseous pollutants from livestock, feed and excretions degrade the air quality in

and around livestock confinement buildings (Hinz and Linke, 1998). Occupational exposures to dust, bioaerosols, ammonia, and hydrogen sulfide in these large-scale facilities received attention in Europe and the U.S. for nearly two decades. Studies of workers document elevated incident levels of asthma, organic dust toxic syndrome, and bronchitis (Thu, 1998). The primary issue in recent studies of neighboring communities focuses on the objectionable odors associated with these operations. Odor investigations detail significant increases in tension, depression, anger, and fatigue in nearby residents (Schiffman, 1995; Hunt, 1998).

Even as the debate continues over the physiological and psychological data, the public concern prompted the State of North Carolina to promulgate permanent rules to control odors from animal operations (DENR, 1999a and b). The rules require operations with persistent problems to implement odor control technologies. As a separate initiative, *Framework for the Conversion of Anaerobic Swine Waste Lagoons and Sprayfields*, proposed by Governor Jim Hunt (1999), requires producers with unresolved problems and new facilities to install new control technologies to minimize emissions.

While North Carolina is at the forefront of efforts to eliminate pollutant emissions from livestock operations, it is not alone. Numerous communities throughout the U.S., Canada, and Europe share in this problem (Thomas, 1999; Smith et al, 1999). The development and full-scale implementation of new technologies to alleviate the adverse effects from the disposal of agricultural waste is imperative. Biofiltration is one such technology under investigation that shows potential as an effective and economic option for treating air emissions and odors from swine facilities.

The objective of this study was to evaluate the technical feasibility and efficiency of ammonia (NH_3) removal from air utilizing biofiltration. A laboratory-scale trickle-bed biofilter was used to nitrify ammonia adsorbed into the biofilm. The biofilter was set up as two columns in series utilizing a patented expanded-clay medium (Infilco-Degremont Biolite^{TM}) and an artificially contaminated and humidified air stream. As components of this objective, the

performance of the biotrickling filter was evaluated as a function of NH_3-N loading rate and the potential use of the medium in a full-scale operation was investigated.

2. LITERATURE REVIEW

2.1 Intensive Livestock Operations

2.1a Recent History in North Carolina

North Carolina experienced an explosive growth in the swine production industry during the last two decades. The hog population increased over 270% since 1990 alone, and exceeds the State's human population (Hog Watch, 1998; DENR, 1999c). This increase is further emphasized as it occurred over a seven-year period prior to the 1997 moratorium on swine production expansion. There were approximately 10 million hogs in the State at the enactment of the moratorium (DENR, 1999c). The hog population at any point in time remained stable at just under 10 million within the restrictions of the moratorium through 1999. Ranked number two behind Iowa among states in the U.S., North Carolina produces approximately one-sixth of the nation's pork (Hunt, 1999; North Carolina Department of Agriculture [NCDA], 1999). While the annual hog production decreased during 1999, quotas still remained near their peak of over 17 million head (NCDA, 1999).

Despite the staggering growth in the hog population, the number of swine facilities has experienced just as dramatic a decrease. The decrease is a result of the closure and consolidation of small family farms, and a move toward large industrial operations that house more than 2,000 head (DENR, Jun. 1999). Since 1970 the number of farms has decreased from nearly 70,000 to a little over 4,000 (Hunt, 1999; NCDA, 1999). The State of North Carolina is currently home to approximately 1,200 major swine facilities housing more than 2,000 swine, with an additional 240 housing more than 1,000 (NCDA, 1999). The recent decline in farm numbers coincidental

with the increase in hog population is illustrated in Figure 1. Large industrial-size facilities are less than 30% of the total number of operations, but raise approximately 98% of the hogs in North Carolina (NCDA, 1999).

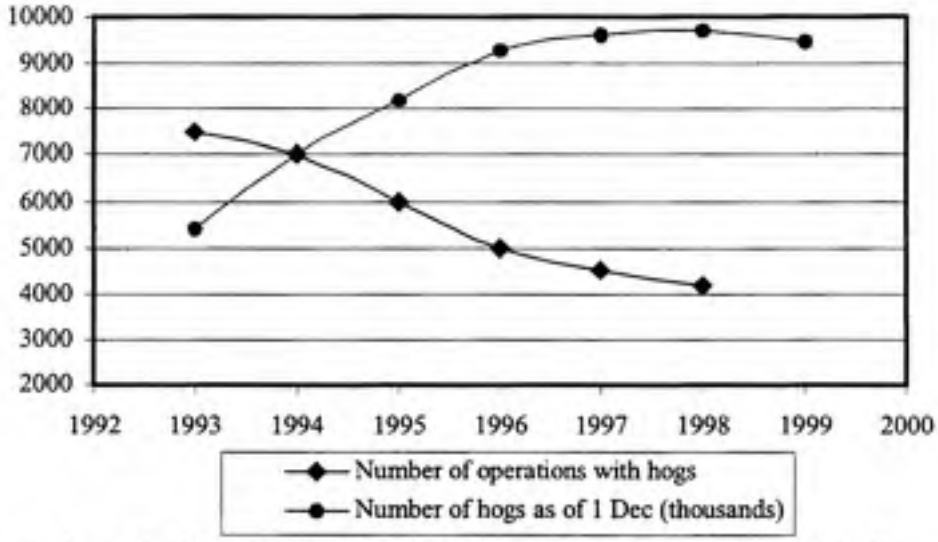


Figure 1. Hog Population and Farm Number in North Carolina, 1992-1999 (DENR, 1999c; NCDA, 1999)

The industrial-scale operations utilize the benefits of "economies of scale" by increasing the number of animals raised per unit area, and decreasing labor costs through the automation of feeding, watering and sanitary maintenance. Enhancing efficiency and bolstering growth rates with antibiotics produces a cheaper and healthier food product. At the same time, they escape federal regulation by the National Pollutant Discharge Elimination System (NPDES), despite the overwhelming quantities of waste that they produce.

The hog population in North Carolina produces an estimated 19 million tons of waste annually, corresponding to 52,000 tons a day (Hog Watch, 1999). This is in addition to the waste generated by 60 million turkeys and 620 million broilers raised in North Carolina each year (DENR, 1999c). The hog operations utilize an estimated 4,000 anaerobic lagoons for the storage of waste prior to sprayfield disposal (Barker and Zublena, 1995; Hunt 1999). Retention times in

these active lagoons are as high as six months, with an estimated 650 inactive lagoons identified by State officials (North Carolina Board of Science and Technology, 1996; Hunt 1999). The long retention times greatly increase the percentage of atmospheric nitrogen emissions from these operations through the volatilization of ammonia in the waste (DENR, 1999c). One U.S. Department of Agriculture report estimates ammonia emissions as high as 80-90% of the nitrogen input to the anaerobic lagoons (Honeyman, 1996). Adding the volatilization from the hog houses and the sprayfields, this estimate rises to 85-95% (Honeyman, 1996; North Carolina Department of Environment, Health, and Natural Resources [DEHNR], 1997).

2.1b Federal Law and Regulations

The majority of the swine waste produced in North Carolina is stored and disposed of using anaerobic lagoons and sprayfields. This long-accepted practice currently satisfies State and Federal Standards. Public concern and disapproval over the last decade prompted the proposal of more stringent laws, regulations, and initiatives at both state and federal levels. Permits required by the Clean Water Act (CWA) authorize the United States Environmental Protection Agency (USEPA) to prohibit point source discharges from Confined Animal Feeding Operations (CAFO) into navigable waters of the U.S., through the NPDES (N.C. Board of Science and Technology, 1996: USDA, 1998; USEPA, 1998). Under the current statute, hog operations with more than 1000 animal units (2500 hogs, weighing more than 55 lbs.) are a CAFO. Operations with more than 301 animal units (750 hogs) may qualify as a CAFO depending on their pollutant discharges (USEPA, 1999). Farms that do not meet these criteria of size or discharge are not regulated. Accordingly, most intensive livestock operations in North Carolina do not require permits, as the lagoon and sprayfield system is a non-discharge system (N.C. Board of Science and Technology, 1996).

New legislation specifically addressing intensive livestock operations is currently in the House Sub-Committee for Water Resources and Environment. The bill previously submitted to

the 105th Congress as H.R.3232, Farm Sustainability and Animal Feedlot Enforcement Act and S.1323, Animal Agriculture Reform Act, was again submitted to the 106th Congress as H.R.684 under the same title. The proposed Act amends the Federal Water Pollution Control Act to make it unlawful, except in compliance with a permit issued under this Act, to discharge pollutants from CAFOs (Thomas, 1999a). The Act contains provisions for air emissions, as discharges are defined to include the release, directly or indirectly, of animal wastes or nutrients, minerals, metals, or other substances derived from animal waste to the waters of the U.S. (Thomas, 1999b). In addition to minimizing the risk of pollutant discharges to water, the Act requires new and existing operations to

> ... eliminate within ten years of such date of enactment, open-air lagoons for the storage of animal waste; eliminate discharges of pollutants to surface water and groundwater; eliminate the atmospheric deposition of nutrients derived from such concentrated animal feeding operations ...; significantly reduce the liquid content of wastes; and promote technologies and production practices that minimize the need for large-scale storage of animal waste (Thomas, 1999b).

Application of animal waste to fields would be considered a discharge of pollutants if the application of nitrogen or phosphorus is in a quantity that exceeds agronomic nutrient uptake. The Act also requires the USEPA to establish minimum setback distances for sprayfield operations from residences and environmentally sensitive locations. All waste storage structures will require closure in accordance with the Act within 180 days of termination of use (Thomas, 1999a). The aggressive bill is receiving stiff resistance in the House Sub-Committee, similar to its predecessors.

2.1c State Law and Regulations

Current management practices approved in the State of North Carolina are similar to the federal statutes, requiring land application of waste at agronomic rates for nitrogen (DENR, 1999c). Additionally, North Carolina regulates air emissions of ammonia in the Toxic Air Pollutant Guidelines, of the Administrative Code (NCAC):

> **15A NCAC Rule 2D.1104**
> A facility shall not emit any of the following toxic air pollutants in such quantities that may cause or contribute beyond the premises (adjacent property boundary) to any significant ambient air concentration that may adversely affect human health. In determining these significant ambient air concentrations, the Division shall be guided by the following list of acceptable ambient levels in milligrams per cubic meter at 77°F (25 C) and 29.92 inches (760 mm) of mercury pressure.... The acceptable ambient level for ammonia is 2.7 milligrams per meter cubed (mg m^{-3}) (NCAC, 1998; Aneja, 1998; DENR, 1999c)

While agricultural operations currently satisfy the requirements of the rule, the wording, "that may adversely affect human health," will remain at the forefront of decisions establishing future acceptable pollutant concentrations.

In the related area of objectionable odors, the North Carolina Environmental Management Commission (EMC) approved a rule to control odors originating from animal operations beyond the operation's boundaries (DENR, EMC, 1999). Temporary odor rules were adopted with an effective date of March 1, 1999 (DENR, 1999a). In accordance with the legislative directive, the rules only apply to operations that house more than 250 hogs and utilize a liquid waste management system. Comparable population limits are in place for other livestock; however, hog farms account for most of the regulated operations. Poultry farms, the other dominant livestock industry in North Carolina, qualify in number (30,000 chickens or turkeys), but generally use dry litter operations (DENR, 1999a). Due to difficulty in measuring the extremely low concentrations of pollutants that produce odors detectable by humans, the EMC did not adopt measurable air quality standards. As a first step, farms need to comply with an EMC approved list of management practices designed to control odors. New and recently modified operations must develop detailed "best" management plans. If odors persist, the rule requires facilities to install odor control equipment such as lagoon covers or wash walls on barn ventilation systems (DENR, 1999a; DENR, EMC, 1999).

Prior to adopting permanent rules, the EMC held a series of hearings to gather input from citizens. Notable changes to the permanent rule approved on 14 October 1999 require detailed

descriptions of odor control measures for all operations, new and existing, meeting size and location requirements. Further, the permanent rule only allows one revision of management practices prior to installing odor control devices (DENR, 1999b). The permanent rule is effective as of July 1, 2000 (DENR, EMC, 1999).

The North Carolina General Assembly (NCGA) approved the extension of the current moratorium on swine facility expansions and new construction. "The Clean Water Responsibility and Environmentally Sound Policy Act," Part I, North Carolina House Bill 515 (1997-1998 Session), signed by Governor Hunt on 27 August 1997, imposed the original moratorium effective through 1 March 1999. North Carolina House Bill 1480, "An Act to Provide for the Registration of Swine Operation Integrators by Swine Growers," signed on 20 October 1998, amended the original bill. The amendment added a section, clarified language, and extended the moratorium through 1 September 1999. The Clean Water Act 1999, Part 2, North Carolina House Bill 1160, signed by Governor Hunt on 21 July 1999, again extended the moratorium through 1 July 2001 (NCGA, 1999).

2.1d State Initiatives

North Carolina's aggressive initiatives to mitigate the adverse effects of the large-scale hog industry extends beyond the Legislature. Early in 1999, Governor Hunt unveiled his *Framework for the Conversion of Anaerobic Swine Waste Lagoons and Sprayfields*. His goal is to achieve a robust swine industry that produces no ill public health or environmental impacts, and becomes a sustainable part of the State's economy. The foundation of the conversion plan as stated in the document: "All swine facilities that fail to protect public health or the environment will be required to convert to new technologies or close out their lagoon and/or sprayfield systems" (Hunt, 1999). The plan requires producers with persistent problems of surface water or groundwater discharges, nitrogen emissions, heavy metal contamination, odors, or public health issues to implement new technologies. The compliance standards are defined in the North

Carolina House Bill 1480. The conversion plan, established with a goal date of 2009, provides financial assistance to farmers and identifies acceptable new technologies (Hunt, 1999).

As part of the conversion plan's directed identification of effective new technologies, the DENR appointed a Technology Panel to head this effort. Projects coordinated by the State Government and Universities are investigating various treatment options that include biofiltration of liquid wastes, sequencing batch reactors, nitrification/denitrification basins, bio-plate composting, covered anaerobic lagoons, and thermophilic (high temperature) digestion (North Carolina State University [NCSU], 1999). As researchers struggle to find effective, economic alternatives to the lagoon and sprayfield system, government officials focus on protecting public health and the environment. As reported by the Associated Press:,

> "The Environmental Management Commission ... giving formal notice that it intends to draft new regulations to operate the waste ponds.... the agency (DENR) is now developing a rating system for risk factors from hog lagoons, while a technology panel studies alternative waste-disposal systems "(Patterson, 2000).

While North Carolina is aggressively addressing the issues associated with intensive livestock operations, the goal of a sustainable industry that is free of adverse public health and environmental impact remains the topic of many debates and may require a number of years to achieve.

2.1e Socioeconomic Considerations

The economic benefits and burdens of the agriculture industry weighs heavy, whether directly or indirectly, in any debate on appropriate action by the State. The agriculture industries contribute much to North Carolina through employment, tax revenue, and subsidiary industries. To the contrary, these industries negatively impact revenue sources such as real estates sales, commercial and sport fishing, and tourism (Duke, 1996). Any solution to the swine waste management problem will cost money. The task before the State is to improve public health and environmental conditions without alienating or destroying the industry.

2.2 Importance of Ammonia Emissions

2.2a Typical Hog Waste Operations

Hog operations produce the majority of their wastewater by flushing excrement from the confinement houses, which minimizes indoor air contamination, waste accumulation, and vector growth. Facilities required to prevent direct discharge of organics, nutrients, and chemical pollutants also collect large volumes of stormwater runoff from feedlots and holding pens. The water from these processes is generally stored in an on-site lagoon. In order to reduce the operation's water requirements, the water is often reused to flush the sub-floor pits in the housing facilities. The flushed wastewater is pumped directly to the lagoon or a sump for temporary storage.

The high concentration of organics and nutrients in the wastewater are metabolized in the lagoon by microorganisms and removed through volatilization and sedimentation. Microbial activity quickly consumes any available oxygen, producing the anaerobic conditions in the lagoon. Since the concentration of nutrients, chemical pollutants, and microorganisms, as well as the lack of oxygen, prohibit direct discharge to water bodies, the wastewater from the lagoons is applied to agricultural fields as a method of final disposal. The application of this no-cost nutrient source also reduces the need for other chemical fertilizers. The wastewater is typically applied to the fields by large, automated spray systems (Cole, 1999).

2.2b Environmental Health

While the common lagoon and sprayfield techniques of storage and disposal satisfy current federal and state requirements, the multi-billion dollar industry is under tremendous public pressure to improve its waste management practices. Research indicates that intensive livestock operations contribute significant amounts of nutrients, heavy metals, suspended solids, and pathogens to ground and surface waters (Duke, 1996). The rapid growth and concentration

of the industry, and subsequent importation of feed, produce an overwhelming nutrient imbalance. Nutrient discharges and atmospheric emissions continue to cause the over-enrichment and eutrophication of surface waters. This stimulates algal growths, leading to sunlight deprivation and oxygen depletion. The decomposition from fish kills and dead riverbed plants furthers the oxygen depletion (Hartung, 1992; Duke, 1996; Madigan, et al., 1997). In 1998, the State of North Carolina documented 107 liquid discharges from swine facilities with 31 reaching surface water. Studies show that 38% of old lagoons leak high levels of nitrogen into the groundwater and 25% of lined lagoons leak to some extent (Hunt, 1999). Some designs actually intend for the lagoons to leak as a method of disposal.

The source of the atmospheric emissions from swine facilities is the volatilization of gases from the animal waste. The gases are products of bacterial decomposition and chemical reactions. The emissions include ammonia, nitrous oxide, hydrogen sulfide, methane, carbon dioxide, and other greenhouse gases (Cole et al., 1999; Hog Watch, 1999). They occur throughout the disposal process, first from the hog houses, then the open-air lagoons, and finally the land application (Hog Watch, 1999). Still, the majority of the volatilization occurs in the open-air lagoons used by 85% of the hog operations in North Carolina (Barker and Zublena, 1995). The most prominent air emission from this storage and disposal process is nitrogen, which is abundantly available for volatilization in swine waste and is often the nutrient controlling argonomic land application rates. Approximately 80% of the nitrogen available in the animal feed is recovered in the waste, and two-thirds of this is in the urine (Kirchmann, 1994). The nitrogen is present in both inorganic (ammonia, NH_3 and ammonium, NH_4^+) and organic forms. The predominant organic form of nitrogen in urine, urea (NH_2CONH_2), quickly hydrolyzes to inorganic ammonia (Kirchmann, 1994). Ammonia is the main source of concern in livestock operations because it is reactive and readily volatilized.

Volatilization is a function of the lagoon's pH, temperature, mixing characteristics and solids content. Research demonstrates that comparing the number of animals served by a lagoon

is not an accurate indicator of the associated emissions (DENR, 1999c). In fact, the production of manure by a type of livestock varies widely and is influenced by animal diet, water intake, feeding regimens, housing environs, and seasonal conditions. For this reason, the manure produced from one farm may vary drastically in composition (Smith et al., 2000; Smith and Frost, 2000).

While nearly 80% of the earth's atmosphere comprises nitrogen gas, it is primarily in a diatomic and almost chemically inert form, N_2 (Madigan et al., 1997; DENR, 1999c). The chemical reactivity and biodegradability of ammonia explain the environmental concern over its emission and subsequent deposition. In addition, the characteristically repugnant smell of ammonia is the primary reason for community odor complaints. Officials in North Carolina estimate that more than two-thirds of the nitrogen in swine waste is emitted to the air as ammonia by volatilization in accordance with the design of the storage and disposal system (Hunt, 1999; Hog Watch, 1999). Other studies report volatile nitrogen losses as high as 80% to 90% (Honeyman, 1996). Table 1 provides annual and daily waste and emissions data compiled from various sources.

Table 1. Hog Waste, Nitrogen Production and Emission Data

Item	Annual	Daily	Source
Waste produced	19,000,000 tons (or 38 billion lbs)	52,000 tons (or 104 million lbs)	Hog Watch, 1999
Nitrogen produced	116,500 tons (or 233 millions lbs)	320 tons (or 640,000 lbs)	Batteye, 1994 Hog Watch, 1999
Nitrogen emitted to air	83,500 tons (or 167 million lbs)	229 tons (or 458,000 lbs)	Hunt, 1999 Hog Watch, 1999
Percent Nitrogen emitted to air	72% 65%-90%	72%	Hunt, 1999 Hog Watch, 1999 Honeyman, 1996

Hog waste alone is estimated to account for over 20% of the total annual atmospheric nitrogen emission in North Carolina and 53% in the eastern portion of the State (Hunt, 1999). Just over 40% of the total nitrogen emissions are as ammonia. Since the livestock nitrogen

emissions are almost entirely as ammonia, hogs account for nearly half of the annual ammonia emissions (Aneja et al., 1998). Numerous studies have verified that ammonia emissions are almost exclusively from agricultural processes (Aneja et al., 1998). An inventory prepared by the European Environment Agency estimated that over 92% of the ammonia emissions in Europe were associated with agriculture. Of this 92%, approximately 80% originated from the decomposition of livestock manure (DENR, 1999c). Current hog waste operations in North Carolina emit more airborne ammonia nitrogen than all other livestock and industrial sources combined (Aneja et al., 1998).

Once in the atmosphere, reactive nitrogen (oxides and ammonia) can increase acid rain, eutrophication, and ozone formation (Hartung, 1992; Aneja et al., 1998). The deposition of the nitrogen is determined by its chemical state, the wind speed and direction, and the ambient temperature and humidity. Nitrous oxides (NO_x), a by-product of combustion processes (boilers and vehicles), has an atmospheric time span of 1 to 15 days (Aneja et al., 1998). Nitrous oxide is a concern because of its role in lower atmosphere ozone formation and acid rain (DENR, 1999c). Ammonia, the major component in eutrophication and a minor player in ozone formation, only remains in the atmosphere for an average of 1-5 days (Aneja et al., 1998; DENR, Jun. 1999). A study of nitrogen deposition in rainfall between 1978 and 1998 showed a threefold increase in ammonia, while nitrate (NO_3^-), remained relatively constant. The stable level of nitrate is attributed to successful regulatory efforts decreasing individual source emissions, which counteracted increases in motor vehicle traffic and industrial activity. The comparatively large increase in ammonia levels is attributed to the explosive expansion of intensive livestock operations (DENR, 1999c).

Gaseous ammonia readily deposits to nearby landscapes, often fields already receiving nitrogen from the aerial spray disposal. A fraction of the airborne ammonia rapidly associates with sulfates to form a fine aerosol. The aerosol particles deposit more slowly than the ammonia gas, travel greater distances, and are primarily removed by rainfall (DENR, 1999c). One study

estimates that 85% of the atmospheric ammonia deposits within 100 kilometers of the source, with dry depositions greatest close to the source and wet deposition (rain) greatest at a longer distance (Duke 1996). On the ground, the ammonia is readily oxidized by nitrifying bacteria to nitrate, which is highly soluble and mobile in the soil and groundwater. Thus, atmospheric deposition of nitrogen and disposal of liquid hog wastes to wet or nitrogen-saturated fields only exacerbates the concern over agricultural runoff. Nitrogen saturation subjects crops to wind and water stress as it promotes shoot growth over root growth, and is likely to induce late season growth rather than plant hardening for the winter (DENR, 1999c).

The effects of nutrient discharge and deposition are clearly evident in the estuaries of North Carolina's Atlantic Coast (Aneja et al., 1998; Hog Watch, 1998; Hunt, 1999; DENR, 1999c). The river basins and estuaries experience algal blooms and fish kills on almost a routine basis. During the last decade while government officials, hog producers, conservationists, and researchers investigated possible solutions for the environment, the focus of concern shifted to the health of neighboring communities.

2.2c Human Health

Occupational. The investigation of adverse health effects in communities neighboring hog farms largely developed from the well-documented research on intensive livestock workers. Since the late 1970s, studies worldwide consistently documented a number of occupational health problems among confinement building workers (Thu, 1998). The increase in confinement housing is a direct result of the advantages of the "economies of scale and concentration," characteristic of expanding industrial operations. By 1996, nearly two-thirds of the swine producers in North Carolina utilized enclosed buildings (Duke, 1996). The accumulation of wastes and bedding in the hog houses can result in the generation of toxic levels of gases and suspended dust particles. Major constituents of the dust include feces, bacteria, pathogens, endotoxins, mites, fungal spores, and animal dander. Prominent gaseous pollutants include

ammonia, methane and hydrogen sulfide, with estimates of between 136 and 160 different compounds in all (Hartung, 1992; Nowak, 1998; Cole et al., 1998; Thu, 1998). Bronchitis, asphyxiation, chronic sinusitis and toxic organic dust syndrome (TODS) are a few of the numerous adverse health effects caused by these pollutants. Table 2 is a compilation of acute symptoms and prevalence rates of illnesses commonly reported by confinement workers.

Table 2. Acute Symptoms and Prevalence Rates of Illnesses Reported by Confinement Building Workers
(Donham and Leininger, 1989; Cole et al., 1998; McBride, 1998; Nowak, 1998; Hog Watch, 1998)

Symptom	Prevalence (%)
bronchitis	70
coughing	67
phlegm/sputum production	56
chronic sinusitis	>50
burning/watery eyes	39
headaches	37
chest tightness	36
toxic orgainic dust syndrome	33
shortness of breath	30
wheezing	27

Factors associated with high concentrations of air-borne pollutants in confinement buildings include poor ventilation in the winter, mixing of manure and urine, high humidity, and elevated temperature. Sustained exposure to ammonia concentrations as low as 25 parts per million by volume (ppm_v) can elicit symptoms such as eye, nose and throat irritation (Cole et al., 1998). Measured ammonia concentrations in swine confinement houses range from 10-50 ppm_v (Cole et al., 1998). The National Institute for Occupational Safety and Health (NIOSH) set a time-weighted average exposure limit of 25 ppm_v (18 mg/m^3) and a short term, 15 minute exposure limit of 35 ppm_v (27 mg/m^3). The Occupational Safety and Health Administration set a short-term exposure limit of 50 ppm_v (35 mg/m^3) (United States Department of Health and

Human Services, 1994). Researchers recommend an ammonia occupational exposure limit in the range of 7 ppm, for confinement workers (Thu, 1998; Schiffman, 1998b).

Recent studies suggest that levels of ammonia emissions from the confinement facilities are similar to emissions from the waste lagoons (DENR, 1999c). The fact that non-confinement workers experience the same symptoms as confinement workers indicates that the exposure to the numerous pollutants generated in these large-scale operations cause symptoms in open-air situations (McBride, 1998). This raises the question of whether the gases and particles from the swine operations induce similar respiratory symptoms in neighboring residents. Plumes of odors can travel several miles, indicating that neighbors are exposed to some unknown extent. The concentration of compounds in the plume may not significantly decrease at distances of over 500 yards (Schiffman et al., 1995). Odor-causing compounds, such as ammonia, present in the plumes also absorb into clothing, curtains, and building materials. Their subsequent release once the plume passes extends the temporal exposure (Schiffman et al., 1995).

Community. Residents, researchers and officials monitor water-borne contamination using widely accepted methods with comparative ease versus airborne pollutants. Nitrate and nitrite, readily formed from ammonia in the soil, can be toxic when ingested, especially by infants. These compounds decrease the ability of blood to carry oxygen, a condition referred to as methemoglobinemia or "blue baby syndrome." Concern about the ingestion of pathogens and antibiotics from animal waste contaminated groundwater is receiving diligent attention in recent studies (Cole et al., 1999). The concern over pathogens also extends to sprayfield operations. The aerosols created during this method of land application significantly increase the dispersion of chemical pollutants and microbial product to neighboring communities. Enteric indicator organisms were isolated from aerosols during spraying of animal waste at cattle and swine farms, at distances of up to 140 yards. The relative risk from these pathogens to the neighboring communities is still under investigation (Cole et al., 1999).

Limited studies report statistically significant increases in acute and chronic respiratory problems in residents near large-scale hog facilities. The symptoms are similar to those of workers from hog confinement operations (Schiffman et al 1998; Cole et al., 1999). Another medical survey reports significantly higher respiratory symptoms for residents living in the vicinity of a large swine operation than neighbors of farms with no livestock (Thu et al 1997, Schiffman, 1998a). Numerous studies verify that environmental odors impact general well-being, affecting both physiological and psychological status (Schiffman et al., 1995; McBride 1998).

In addition to the symptoms identified by workers, exposure to repugnant odors in the home result in significantly more tension, depression, anger, and fatigue (Hog Watch, 1998). One study suggests that in extreme cases, offensive odors "lead to deterioration of personal and community well-being, interfere with human relations, deter population growth and lower its socio-economic status" (Shukla, 1991). A direct link between unpleasant odors and elevated stress, immunity suppression, performance impairment, and negative-Pavlovian response is supported by the positive effects from aroma-therapy (Schiffman, 1998).

A recent study of North Carolina communities near swine, cattle and non-livestock farms identified quality of life as the largest difference among the communities. More than half of the respondents in the community near a hog farm reported not being able to open windows or go outside during nice weather 12 or more times over a six month period. Fewer than 20% of the respondents reported the same conditions in other communities (Wing, 2000). This study supports the statement of Dr. McBride:

> ... as a preventive public health policy, the State Health Director (McBride) considers exposure to hog farm odors as a public health risk and recommends that efforts be made to minimize odor exposures. The State Health Director encourages farm owners/operators and regulators to take actions to minimize odor and inhalation exposures of hog farm workers and hog farm neighbors (McBride, 1998).

Physiology. The adverse physiological adverse effects of exposure to the combined and individual odorous compounds in the gaseous plumes emitted from industrial operations are well documented in numerous fields. The adverse effects on farm workers are irrefutable, as discussed above. Research in recent years has focused on the less defined aspect of odor. Odor is the sensation perceived through smell and involves the activation of at least one of five different cranial nerves (Schiffman et al., 1998; Schiffman 1998b). The two primary nerves, located in the nose, control the two base characteristics of an aroma (Schiffman, 1998a). The olfactory nerve distinguishes between odors, allowing one to determine the difference between meat and vanilla for example. The trigeminal nerve mediates the nasal pungency and irritation, as in pepper and ginger (Schiffman et al., 1998; Schiffman, 1998a). Compounds induce both odor and pungency above certain threshold levels and may be hyperadditive (Schiffman, 1998b). Ammonia produces irritation at a level above but within an order of magnitude of odor threshold or detection (Schiffman et al., 1998). Studies also report health symptoms from exposure to odors at three to four orders of magnitude below irritant thresholds (Schiffman, 1998a). Research suggests that these symptoms result from non-toxicological mechanisms such as innate odor aversion, pheromonal phenomena, exacerbation of conditions and recall bias (Schiffman, et al., 1995; Schiffman et al., 1998; Schiffman, 1998a). As the direct link between odor and adverse health effects is validated by such investigations, odor removal performance may become a primary objective of future research on treating air emissions from swine facilities.

2.2d Outlook

As the evidence of adverse physiological and psychological effects on neighboring communities continues to develop, the swine industry is under increasing pressure from the public to adjust their practices to protect the health of the local community and environment. In general, animal waste is an excellent resource for soil fertilization and conditioning, but it will

require more stringent management practices to achieve public acceptance. The successful management of the waste may lie in the development and application of new technologies.

Treatment of ammonia through a nitrification/denitrification process could reduce the volatilization of ammonia and associated odors from manure and liquid wastes, as well as reduce the nitrogen load in liquid wastes prior to discharge or land application. Subsequently, this would reduce the over-enrichment of surface waters and the concentration of nitrite and nitrate in the groundwater resulting from atmospheric nitrogen deposition and land application of the waste (Cole et al., 1998). This natural biological process of nitrification/denitrification is one of the cornerstones of biofiltration technology. Use of biofilters in conjunction with confinement house ventilation systems and manure storage facilities can potentially remove the majority of pollutant gases and particulates. The potential multi-purpose treatment benefits make biofiltration an attractive option (Li, 1997).

2.3 Emergence of Biofiltration

2.3a A Treatment Option

Biofiltration is the most frequently used biological treatment process to reduce air pollution (Morales et al., 1998). In general, the use of biofiltration falls into one of three categories: treatment of odors, treatment of volatile organic compounds (VOCs) and treatment of hazardous air pollutants (HAPs) (Devinny et al., 1999). These pollutants are common in emissions from industrial processes, commercial operations, and waste treatment systems. Contaminant concentrations range from parts per billion to several thousand parts per million by volume, depending on the source. Biological air treatment was first used for the purpose of odor control and is commonly employed at wastewater treatment plants (Amirhor et al., 1995; Kinney et al., 1998; Li, 1998).

The use of a biological treatment system to eliminate ammonia and odors from intensive livestock operations presents many implementation options. In addition to treating the air from ventilation systems of the confinement houses, stripping towers could transfer ammonia in the wastewater removed from the sub-floor manure pits to the gas phase. Treatment of volatilized emissions from lagoons, while a structural challenge, is also a possibility. After collection, the waste gas could be treated in a biofiltration system to convert the objectionable components into acceptable products. Some products may require additional conversion in subsequent stages, as is the case with ammonia oxidation through nitrification. Once the ammonia is converted to nitrite (NO_2^-) and nitrate (NO_3^-), a second reactor could be used to denitrify the products to nitrogen gas (N_2) for safe release to the atmosphere.

2.3b History and Description

Microbial reactions were used throughout the twentieth century to treat liquid and solid wastes (Devinny et al., 1999). European scientists proposed biofiltration of air as early as the 1920s to control emissions of hydrogen sulfide and other odorous compounds (Morales, 1998; Devinny, 1999). It was during the 1950s that such techniques were implemented to treat odorous compounds in low concentrations. In the 1960s, research continued and plants installed biofiltration to treat gaseous pollutants. The enactment of strict air quality regulations during the 1970s expanded research and development in biofiltration, as the new regulations often pushed beyond the capabilities of existing biofilters. Successful use of biofiltration to clean the air in West Germany and the Netherlands was hindered by poor stability (Devinny et al., 1999; Devinny, 1999).

The mid-1980s witnessed extensive commercial application of biofiltration in Europe (Kinney et al., 1998). German and Dutch industries started using biofiltration to control VOCs and HAP emissions (Devinny, 1999). Research and application of biological gas treatment made large advances in the U.S. during the 1990s. Today computer-operated, enclosed systems

utilizing natural and synthetic media successfully reduce or eliminate odors, VOCs, and various mixtures (Morales et al., 1998; Devinny et al., 1999). The process is still most effective for odor control, but is finding additional application for VOC removal. One study estimates that the primary function of 78% of installed biofilters is for odor control, 14% for VOC removal and 8% for mixed purposes (Morales et al., 1998). Improvements in stability, relative simplicity, and low cost operation continue to expand the biofiltration market. There are more than 500 full-scale biofilters treating waste gas in Europe alone (Kinney et al., 1998; Devinny, 1999).

Biofiltration uses microbial metabolic reactions to treat contaminated waste gas. Under optimum conditions, the reactions oxidize and/or reduce organic pollutants such as hydrocarbons and other VOCs, and inorganic air toxics such as hydrogen sulfide or ammonia, to carbon dioxide, water, salts and organic biomass. In most cases the microbial community uses the air contaminants as a source of energy and carbon for maintenance and growth activities. As such, the contaminants must be biodegradable and non-toxic. The conversion, or degradation, of the compounds occurs as the waste gas passes through a porous, biologically active material. generally referred to as the bed or media. The pollutants transfer from the air into the active microbial layer, or biofilm, which develops on the media particles. These gas-phase reactors are most successful at removing low molecular weight, highly soluble compounds with simple bond structures (Morales et al., 1998; Devinny et al., 1999; Devinny, 1999).

Biofiltration relies on a combination of natural processes: adsorption, absorption, desorption and degradation. Furthermore, it generally uses naturally occurring microorganisms. The microorganisms create and live in communities within the biofilm on the surface of the media or in the water phase surrounding the media. The microbial communities vary in diversity from near mono-cultures to robust systems including bacteria, fungi, protozoans and invertebrates (Kinney et al., 1998; Devinny et al., 1999). The factors influencing the growth of these communities within the bed include media characteristics, moisture content, nutrient supply, pH, and temperature.

The filter media generally consists of relatively inert substances and is selected based on its ability to support the desired microbial community. Media materials fall into two broad categories, natural and synthetic. Natural media includes soil, peat, and compost. Compost is the far most common because of its high porosity, high surface to volume ratio, diverse and active microbial population, and available trace nutrients. Compost and peat media often require the use of a bulking agent such as perlite, rice hulls or vermiculite to maintain the porous structure of the bed (Kinney et al., 1998). Examples of synthetic media include extruded diatomaceous earth pellets, polypropylene pall rings, expanded polystyrene spheres, sintered glass disks, and granular activated carbon (GAC). As is the case with the natural media, the porous structure of synthetic media such as diatomaceous earth pellets, sintered glass, and activated carbon, makes it desirable due to its high surface to volume ratio compared to nonporous materials. The media are usually irregularly shaped and porous, ensuring large surface attachment areas and nutrient supply. Still the use of uniform, synthetic media such as pall rings and gridded packing continues to be investigated (Kinney et al., 1998).

Two general categories are used to classify biofiltration systems: biofilters, in which nutrients are primarily stored in the media; and biotrickling filters or trickle-bed biofilters, in which nutrients are provided by an external source of water that is supplied to the system continuously or semi-continuously. The bacteria within the biofilm, which account for the majority of the biological activity in the filter bed, obtain all of their nutrition from the liquid phase in either case. The contaminants that absorb into the liquid film diffuse into the biofilm, where they serve as metabolic sources of energy, carbon or inorganic nutrients. The liquid film coating the biofilm is usually very thin, on the order of 20 μm. Experimental data suggest that the transport of pollutants across the liquid film is rarely the rate-limiting factor (Kinney et al., 1998). Consistent with this theory, the kinetic reactions are based on a two-phase (gas – biofilm) model as opposed to a three-phase (gas – liquid film – biofilm) model.

Proper moisture control is obviously a paramount consideration for successful contaminant removal in biofiltration. Moisture content is maintained during operation by passing the waste gas through a humidifier to achieve water saturation. Some systems also heat the waste gas upstream of the biofilter to produce condensation from the cooling of the gas within the reactor. Industrial waste gas streams are often already elevated in temperature and do not require the heat augmentation. Most biofiltration systems operate in the temperature range of 15 to 40°C, which supports the optimum growth of bacteria common to these systems (Kinney et al., 1998). Biotrickling filters and many biofilters also utilize a continuous or intermittent water source to maintain the moisture level. The supplemental water provides a convenient way to add nutrients required by the microbial community. In addition, the free water removes potential toxic or inhibitory degradation by-products, transfers biomass through the bed for continuous reseeding, and aids in the diffusion of hydrophilic pollutants, such as ammonia, into the biofilm (Devinny et al., 1999).

The microbial communities within a biofilter treating organic contaminants often require nitrogen, phosphorus, and trace elements such as sulfur, iron and magnesium in quantities exceeding that available in the contaminated gas. While natural media usually contains sufficient amounts of the trace elements, most filters require the addition of nitrogen and phosphorus. Biofilters designed to utilize autotrophic bacteria to treat contaminants, as is the case with nitrification, may also require inorganic carbon. The addition of carbonate or bicarbonate, while providing the necessary carbon for cell synthesis, can serve as an excellent buffer for the control of pH. Since the biofilm contacts the liquid film, control of the liquid phase pH directly impacts microbial growth and metabolism (Kinney et al., 1998). Most naturally occurring bacteria used in biofiltration systems grow best in the pH range of 6 to 9. Understanding of the effects of pH, temperature, moisture control, media characteristics, and nutrient supply has advanced the overall treatment efficiency and stability of biofiltration.

2.3c Operational Control

Biofiltration systems are subject to numerous operational difficulties relating to five primary concerns: moisture, pH, and temperature control; nutrient limitation; and biomass accumulation. Biotrickling filters and biofilters are open systems, and as such, it is virtually impossible to absolutely define the composition of the microbial community. Generally, biotrickling filters are easier to control than biofilters with regard to system pH, nutrients, salts, and tolerance of differing hydraulic and nutrient loads (Webster et al., 1999; LeKang and Kleppe, 1999). Biofiltration systems are often designed and operated to support a particular growth environment based on the treatment needs, which allows for a relatively accurate prediction of system's performance and potential inefficiencies.

Moisture control. Since the bacteria in the media obtain all their nutrition from the liquid phase, proper maintenance of the liquid film through moisture control is imperative. In addition to providing the biofilm a means to receive nutrients, the water of the liquid film is often required for microbial metabolism. Inorganic natural media require less moisture than organic media, as they have a lower bound water fraction. The water in organic media is bound tightly to the media and requires a high amount of energy to make it available for metabolism (Bohn and Bohn, 1999).

Maintaining bed moisture content in natural media filters is particularly important because excessive drying often results in crack formation and channeling in the bed. Channeling affects both the liquid and the gas flow distributions (Kinney et al., 1998; Devinny et al., 1999). Spatial variations in the bed resistance from the initial channeling promote further channeling and limit performance. The diversion of contaminated air and supplemental nutrients, and the lack of an adequate liquid film may lead to the development of dead zones within the media bed (Morales et al., 1998; Bohn and Bohn, 1999).

While bacteria are more moisture tolerant than drought tolerant (Bohn and Bohn, 1999), excessive moisture is also detrimental (Kinney et al., 1998; Devinny et al., 1999). An excess of

water may result in clogging or a washout of the bacteria. Clogging promotes channeling, reduces the gas transfer contact area, develops anaerobic zones and increases head loss. Head losses in media beds can vary from 25 mm of water to 500 mm of water (Kinney et al., 1998). Local anaerobic zones may generate nutrient losses - the denitrification of nitrate to nitrogen gas is one example if nitrate were being used as a nitrogen source. Routine monitoring of moisture content, bed humidity, and filter performance usually identifies potential problems with moisture control. New designs include liquid spray systems and deep plenums to promote good flow distributions to further prevent channeling and clogging (Morales et al., 1998; Bohn and Bohn, 1999).

pH control. The metabolic reactions and by-products of the microbial community can have dramatic effects on the performance of a biofiltration system. Biofilters treating waste gases contaminated with sulfides or halogenated compounds encounter significant problems with bed acidification and corrosion (Kinney et al., 1998; Devinny et al., 1999). Nitrifying systems can also experience similar acidification to a lesser degree without deliberate operational control. Carbonate and phosphate species are commonly used to buffer biofiltration systems.

The effects of hydrogen (H^+) and hydroxide (OH^-) ions on metabolism, inorganic carbon speciation and the concentration of potential inhibitors define the optimum pH range for biofiltration (Villaverde et al., 1997a). The pH also affects the chemical equilibrium of carbonate (CO_3^{-2}, HCO_3^-, CO_2), in turn impacting the availability of carbon, especially for autotrophic bacteria. At a low pH, stripping eliminates the predominant species CO_2 (from H_2CO_3). At a high pH, carbonate dominates, but is characteristically insoluble and difficult to assimilate (Snoeyink and Jenkins, 1980; Villaverde et al., 1997a). Just as pH adjusts the equilibrium concentration of the carbon species, it adjusts the concentration of various ionizable biological inhibitors in an identical manner. All of these effects occur simultaneously with changes in the liquid phase pH. Fortunately, the processes are reversible and the overall performance of a biofilter can be improved with an adjustment of the pH (Villeverde et al., 1997a).

Temperature control. Similar to pH, temperature directly affects microbial growth and metabolism. Dramatic, short-term temperature changes can lead to extreme effects on removal rates and may permanently damage the microbial community. Long-term temperature variations can promote microbial adaptation to the new conditions or dominance of new species (Kinney et al., 1998). As an exothermic reaction, the oxidation of ammonia may significantly warm the media. The heat released is proportional to the contaminant concentration and its Gibbs free energy (Bohn and Bohn, 1999). An increase in the bed temperature promotes drying and the associated problems discussed above (Fdz-Polanco et al., 1994; Morales et al., 1998). Auxiliary heating and cooling systems are generally incorporated into the design of the biofilter to eliminate the large variations in temperature and the corresponding problems.

Nutrient limitation. Prolonged nutrient limitation results in the cessation of microbial growth and metabolism. While dramatic short-term changes in the nutrient supply may affect removal rates, even after the supply is restored, most healthy microbial communities do not experience permanent damage. Contrary to temperature effects, nutrient limitation affects the community more gradually, as many organisms are capable of sustaining themselves on intracellular nutrient stores, nutrient desorption from the media and dead cells. Similar to temperature, long-term variations can promote microbial adaptation to the new conditions or the dominance of new species.

The addition of specific nutrients helps to maintain or improve biological degradation rates for systems treating high loadings or specific pollutants (Morales et al., 1998). Phosphorus is typically the limiting nutrient in nitrifying systems. The addition of a proper phosphate compound not only provides the required nutrient, it acts as an effective pH buffer comparable to the carbonate species. Nitrifying biofiltration systems may experience other nutrient limitations due to volatilization of ammonia, stripping of CO_2, and storage of nitrogen in humic materials. If nitrate or nitrite are used as a nitrogen or energy source and anaerobic areas develop, or if the

waste gas is oxygen deficient, denitrification can consume available nitrogen (Kinney et al., 1998).

Biomass accumulation. Biofiltration units are susceptible to clogging with biomass unless control measures, most commonly backwashing of the media bed, are used to control biomass accumulation. Internal pores smaller than 10 μm are subject to rapid plugging with microbial growth (Hagopian and Riley, 1998; Kinney et al., 1998). When plugging occurs, the cells on the inner portion of the particles only receive the contaminant nutrients by diffusion through the microbial mass. Diffusivity through the biofilm is approximately three orders of magnitude lower than through air. The resultant concentration gradient and overall removal efficiency are lower because of the decreased availability of the waste gas within the media.

The different rates of diffusion not only impact a species population density, but also influence the location and order of populations within the media bed. The concentration, chemical composition and diffusivity of a chemical contaminant all contribute to microbial stratification (Nijhof and Klapwijk, 1995; Kinney et al., 1998). Compounds that are rapidly transported and easily degraded are quickly removed from the gas stream. Microorganisms that most readily utilize these compounds thrive in the influent section of the bed. Waste gas compounds and degradation products that are less rapidly transported and less degradable move farther into the column. Thus, microorganisms that most readily utilize these compounds develop later in the column (Nijhof and Klapwijk, 1995; Madigan et al., 1997; Kinney et al., 1998).

In general an increase in the loading rate increases growth, and subsequently broadens the accumulation of biomass in the media. The rise in the microbial population density usually originates in the influent section of the bed. Once the media pores are plugged, the greater density profile may move further into the column. As a result, the initial section of the bed may experience a decrease in performance below that prior to the biomass accumulation due to channeling and slower diffusion through the biofilm. Still, the bacterial penetration into a larger portion of the bed can have beneficial consequences if the biofilter experiences routine

fluctuations in pollutant concentrations. The added biomass increases the potential reaction capacity above that required by the lower steady-state loading. The excess capacity provides the biofilter resilience to respond to elevated concentrations (Kinney et al., 1998). Biofiltration systems designed to promote nitrification are able to maintain the excess growth because of the nitrifiers' ability to survive starvation and anaerobic conditions (Hagopian and Riley, 1998).

2.4 Nitrification

2.4a Microbiological Process

Nitrification is the two-step microbiological oxidation of ammonia to nitrite, and then to nitrate. Two distinct groups of bacteria accomplish this process. Collectively they are known as "nitrifying bacteria." The ammonia oxidizing microorganisms include bacteria of the genera *Ntirosomonas, Nitrosococcus, Nitrosospira, Nitrosolobus,* and *Nitrosovibrio*. The nitrite oxidizing microorganisms include bacteria of the genera *Nitrobacter, Nitrospina, Nitrococcus,* and *Nitrospira* (Madigan et al., 1997; Hagopian and Riley, 1998). All of the bacteria are Gram-negative chemoautotrophs, also known as chemolithotrophs. They utilize the ammonia or nitrite for energy and synthesis (Villaverde et al., 1997b; Hagopian and Riley, 1998). The bacteria are aerobic, using oxygen as the terminal electron acceptor. Carbon dioxide (CO_2) and oxygen (O_2) are consumed as a result of metabolism. Equations 1 and 2 represent the basic steps in nitrification and provide the corresponding energy released (Michette, 1996; Madigan et al., 1997; Hagopian and Riley, 1998).

$$\mathbf{NH_3^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + H^+} \quad \Delta G^\circ = -84 \text{ kcal/mol} \quad (1)$$

$$\mathbf{NO_2^- + 0.5\ O_2 \rightarrow NO_3^-} \quad \Delta G^\circ = -17.8 \text{ kcal/mol} \quad (2)$$

Since microbial growth is a function of the pH, temperature, salinity, concentrations of substrate and dissolved oxygen, and hydrodynamics (Fdz-Polanco et al., 1994 and 1996;

Villaverde et al., 1997a; Michette, 1996; Hagopian and Riley, 1998; Gyhoot et al., 1999), nitrification is a function of these parameters. Most of these parameters influence both the nitrogen speciation and microbial activity. In general, nitrite oxidizers are more susceptible to pH and temperature changes, and lower oxygen concentrations, than are ammonia oxidizers (Fdz-Polance et al., 1994; Michette, 1996; Villaverde et al., 1997a).

Nitrifying bacteria prefer attached growth systems. Their affinity for adhesion is such that between 70 and 95% of a suspended community will attach to fine inert media within 30 minutes of its introduction to a liquid medium (Hagopian and Riley, 1998). If sufficient surface area is unavailable, the nitrifying community will form loose flocs (Madigan et al., 1997; Hagopian and Riley, 1998). Higher metabolic activity and viability are recorded in attached communities compared to suspended communities under the same conditions (Hagopian and Riley, 1998). Complementary metabolism (syntrophy) and consistent conditions explain the preference and superior performance of nitrifying bacteria for attached growth systems.

As is expected, performance varies between systems and different waste streams. Trickling filters used to treat liquid wastes usually produce lower nitrification rates than other types of biofilters. Typical nitrification rates for systems designed and operated to remove ammonia range from 0.01 to 2.0 g total ammonia nitrogen (TAN)/m^2_{media} d (Lekang and Kleppe, 2000). Nitrification rates of 1.6 to 2.1 g N/m^2 d were reported for a trickling filter operated as a single stage and as a two stage alternating series system, respectively (13-15 °C) (Anderson et al., 1994). Performance also varies spatially, temporally and biologically within a system, as well as being dependent on the mode of operation. This is particularly true during start-up periods, as ammonia oxidizers typically have a higher growth rate than nitrite oxidizers (Ghyoot et al., 1999).

Biofilters receiving a sudden increase of ammonia may experience constant effluent levels of nitrite or increases in nitrite consistent with the influent ammonia changes (Nijhof and Klapwijk, 1995). Such changes in performance are largely dependent upon the spatial location and density of the microbial community defined by the operational conditions. If the fluctuation

is routine, the systems may be able to accommodate the ammonia increase, consistent with bacterial over-growth discussed above. If the increase is uncommon, such as a spill event, the system is likely to overload the system's capacity. Additionally the elevated ammonia concentrations may lead to further accumulation of nitrite because of inhibition of nitrite-oxidizing bacteria.

2.4b Nitrite Accumulation

Mass Transfer. Elevated nitrite concentrations in biotrickling filters are often entirely explained by diffusion and biofilm characteristics. Biofilm mass transfer is up to three times slower than air phase transfer and published data confirm that transport through the liquid film is rarely the limiting factor (Kinney et al., 1998). Within the biofilm, nitrite oxidation is the rate-limiting step. Ammonia oxidizers cope with increases in loading better than nitrite oxidizers, due in part to their higher specific growth rate and their higher saturation constant for ammonia, $Ks_{,NH}$ relative to Ks_{NO2} for nitrite oxidizers (Madigan et al., 1997; Gyhoot et al., 1999).

This difference in nitrite production and consumption results in elevated levels of nitrite within the biofilter, at least temporarily. Since the nitrite isn't immediately utilized in the biofilm, it diffuses into the bulk liquid and is transported further into the bed (Figure 2) (Nijhof and Klapwijk, 1995).

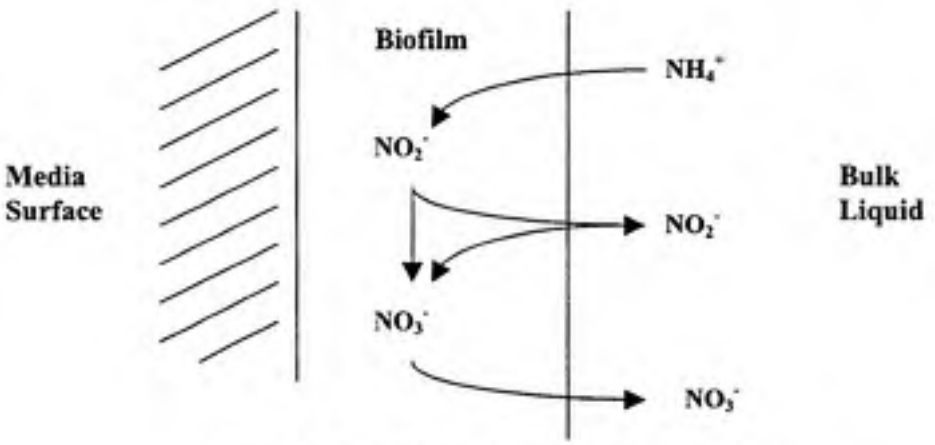


Figure 2. Nitrite Mass Transfer within a Biofilm.

The transport of the nitrite sustains the development of a relatively homogenous density of nitrite oxidizing bacteria throughout the media. This is apparent by the elevated nitrite levels found in the initial portions of a biofiltration bed, even though the system's overall performance may remain unchanged.

Inhibition. Ammonia and nitrite are common inhibitors of nitrifying bacteria in their un-ionized forms, NH_3 and HNO_2 (Table 3). Ammonia and nitrous acid concentrations are a function of pH, temperature, and the concentrations of their ionized forms. In water, the ammonia species exist as either the ammonium cation NH_4^+ or the neutral free ammonia NH_3, as given in Equation 3 (Villeverde et al., 1997b). The ratio of NH_3: NH_4^+ increases with pH and temperature (Michette, 1996). With a pKa of 9.3, ammonium is the dominant species under neutral conditions (Snoeyink and Jenkins, 1980). In contrast the protonation of nitrite to nitrous acid increases with decreasing pH, having a pKa of 4.5. Since ammonia is of direct concern in this study, an equation used to estimate liquid phase ammonia concentrations is presented in Equation 4 (Villeverde et al., 1997a; Hagopain and Riley, 1998).

$$NH_4^+ + OH^- \leftarrow \rightarrow NH_3 + H_2O \qquad (3)$$

$$[NH_3\text{-}N] = ([NH_4^+\text{-}N] \cdot 10^{pH}) / (\exp(6334/273 + T) + 10^{pH} \qquad (4)$$

Table 3. Relevant Nitrification Inhibitors (Hagopian and Riley, 1998)

Inhibitor	Concentration Range	Process
Ammonia	NH_3 > 10 - 150 mg/L	Ammonia Oxidation
Ammonia	NH_3 > 0.1 - 1.0 mg/L	Nitrite Oxidation
Nitrous Acid	HNO_2 > 0.22 - 2.8 mg/L	Nitrite Oxidation

The concentrations of ammonia in Table 3 suggest that nitrite oxidizers are much more sensitive to inhibition than are ammonia oxidizers. Partial inhibition of nitrite oxidizers is possible above pH 7.0. Since the ammonia oxidizers are less sensitive to inhibition, ammonia would be consumed and its concentration would decrease as it proceeds through a packed bed.

This allows nitrite oxidation to continue, and occasionally increase, deeper in the filter (Villaverde et al., 1997a and b; Nijhok and Klapwijk, 1995).

The complete conversion of ammonia to nitrogen gas includes the anaerobic process of denitrification. While denitrification was not studied in this project, implementation of nitrification as an effective treatment often requires its complementary use. Nitrogen removal is accomplished through either the nitrite pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2$) or the nitrate pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$). Since the nitrite pathway requires less oxygen, time and consequently space, controlled inhibition of nitrification presents potential advantages. However, the ability to sustain nitrite accumulation indefinitely is improbable, as it is difficult to avoid acclimation of the nitrite oxidizers to the ammonia (Gyhoot et al., 1999)

2.5 Ammonia Removal

The primary air contaminant in this laboratory study was ammonia. The processes used to remove ammonia from a waste gas include carbon adsorption, wet scrubber, and incineration. The combined capital and operational cost of these methods, including disposal of secondary pollutants, is relatively expensive compared to biofiltration. Biofiltration is a proven effective treatment option, especially for dilute biodegradable gases (Chung et al., 1997; Chung and Huang, 1998; Webster et al., 1999). Still, limited applications have focused on the removal of ammonia from an air stream using a biotrickling filter (Westerman et al., 1998). Comparative values for optimum pH, temperature, ammonia concentrations, and loading rates, from studies using aerated biofilters and biotrickling filters for wastewater treatment were therefore reviewed for guidance. Performance results and other related issues are discussed in this section.

2.5a Optimum pH and Temperature

Studies agree that an operational pH range between 7.0 and 8.5 is optimum for ammonia and nitrite oxidizing microorganisms. Chung and Huang (1998) identified an optimum pH of 7.5

for ammonia oxidation in a biofilter by the chemoautotrophic *Nitrosomonas europaea*. Variations in optimum pH and temperature varied slightly depending on the microbial community. A maximum specific growth rate of 0.04 hr^{-1} was determined at this optimum pH. The growth rate dropped to 25% of the maximum at pH 6.5 and to zero at pH 6.0. The drop in growth rate was attributed to the increasing scarcity of ammonia associated with the lower pH. The *N. europaea* biofilter was more tolerant of alkaline conditions. The growth rate only decreased to 75% of the maximum at pH 8.5 pH (Chung and Huang, 1998). Villaverde et al., (1997) reported a 13% increase in nitrification efficiency for every unit increase of pH within the range of 5.0 to 8.5, indicative of a broader community of nitrifying bacteria. They also reported the highest activity of ammonia oxidizers and highest values of volatile attached solids (VAS) in the filter at pH 8.2.

Additional studies identified an optimum temperature for nitrifying bacteria between 20 and 35°C (Fdz-Polanco et al., 1994 and 1996; Villaverde et al., 1997a; Hagopian and Riley, 1998). This agrees with the 30°C optimum temperature and greater than 93% removal efficiencies obtained by Chung and Huang (1998) in this range. A temperature decrease to 15°C only dropped the removal efficiency to 78%. However, the efficiency decreased to 25% at a temperature of 45°C (Chung and Huang, 1998). Hagopian and Riley (1998) identified rapid decreases in nitrification at temperatures of 42°C and 5°C. A pilot plant biofilter witnessed a reduction in its total ammonia removal from 94% to 52% during the seasonal change from summer to winter (Westerman et al. 1998).

2.5b. Ammonia Concentration and Loading Rate.

In a biofiltration system for gas treatment, the contaminated air is the primary fluid of concern. Waste gas characteristics such as ammonia concentration and loading rate influence the system's overall performance. However, in principle, loading rates for gas-phase biofilters should be comparable to those for wastewater treatment systems if the contaminants are readily

soluble in water. An increase in the hydraulic load on an up-flow biological aerated filter (UBAF) used to treat a liquid phase contamination of ammonia had little influence on performance (Villaverde et al., 1997b). An increase in the influent ammonium concentration in the same biofilter decreased the nitrification efficiency, while increasing the ammonia removal rate. Table 4 presents data collected in this study.

Table 4. Nitrification Efficiency and Ammonia Removal Rate for Increasing Influent Influent Ammonium Concentrations In a Upflow Biological Aerated Filter (UBAF) (Villaverde et al, 1997b)

Concentration g N / m3	Efficiency removal %	Removal Rate kg N / m^3 day
50	95	0.51
75	81	0.65
100	72	0.77
150	65	1.05

Studies have also attempted to relate ammonia and odor removal. A performance test conducted to evaluate biofilter efficiency in removing odor and odorous compounds from a biosolids composting facility found a 80% to 90% decrease in subjective odors coincident with a 98% removal of ammonia (Amirhor et al., 1995). A study by NCSU reported a significant reduction in odor intensity and irritation from flushed swine manure following treatment in an aerobic fixed media biofilter designed to remove ammonia from the liquid waste (Westerman et al., 1998).

2.5c Media

Overall biofiltration system performance is directly influenced by media characteristics as well. The most important aspect of a biofilter/biotrickling filter design is the selection of a proper medium. Specific characteristics of concern include void ratio, surface area, weight, water flow, pollutant adsorption, bacteria compatibility, and economics (McNevin et al., 1999; Bohn and Bohn, 1999, Devinny et al., 1999; Lekang and Kleppe, 2000). A liquid-phase study

conducted to determine the effects of media type on nitrification reported removal efficiencies between 100% and 57% (Lekang and Kleppe, 2000). The best performance was obtained with a light-weight clay aggregate (Leca™) and corresponded to a total ammonia consumption of 1.3 mg/L from the influent contaminated water. The best performance by a plastic medium was obtained with Kaldnes rings at 80% removal. The plastic media required the least amount of oxygen because of their larger void ratios. Complete oxidation of ammonia to nitrate requires 4.57 mg O_2/mg NH_4^+-N. Interestingly, the plastic media with the worst overall nitrification efficiency obtained the best nitrification capacity per unit retention time of the liquid in the media bed.

The available surface area in any biofilter process influences the concentration of biomass in the reactor, which in turn influences the achievable contaminant removal rates. Typical media surface areas range from 6 to 10 m^2/g and 60 to 165 m^2/m^3 (Kinney et al., 1998; Westerman et al., 1998). The available surface area may become significantly reduced over time because of biomass accumulation and subsequent clogging of internal pores. However, the relatively low biomass growth yields typical of nitrifying bacteria (Nijhof and Klapwijk, 1995; Madigan et al., 1997; Villaverde et al., 1997b) reduces the likelihood of this potential problem.

The high pollutant adsorptive capacity of some media beds provides significant buffering to aid in countering surge and starvation loading rates. One study reported that the mass transfer of ammonia from the liquid film to the solid surface was virtually instantaneous compared to the solute bulk transport having a mean residence time of approximately 10 minutes (McNevin et al., 1999). Based on this finding, the mass transfer resistance opposing adsorption and degradation was discounted as negligible. The study also concluded that the biological degradation of the ammonium was slower than the mass transfer. Thus, media with a sorptive capacity may be able to accumulate or release ammonia to the aqueous biofilm depending on the ammonia concentration of the bulk liquid.

2.5d Moisture Availability

The composition, size and shape of the media also determine the relationship of water availability to moisture content. A study by Bohn and Bohn (1999) found that biofilter water availability rather than water content affects the metabolic rates of microbes. Water availability is expressed as either a water activity or water potential. The water activity equals the relative humidity of the air and ranges between zero (dry) and one (free water). Activities between 0.999 and 0.97, and potentials from -0.2 and -3.0 bars (-20 to -300 kPa), supported high microbial degradation rates. In this study, the microbial activity slowed rapidly if the humidity in the biofilter dropped below approximately 96%.

The energy of water retention in a medium increases exponentially as the water content decreases, emphasizing the need to keep the bed moist. Microbes must overcome this energy in order to utilize the water for metabolism. As a general rule, organic media beds with a 50-60% moisture content, wet weight basis, provide good performance (Kinney et al., 1998; Bohn and Bohn, 1999; Devinny et al., 1999). Inorganic media moisture requirements depend to a greater extent on the particle size distribution. Bohn and Bohn (1999) also confirmed that the hydraulic properties of porous media prevent an equal vertical moisture profile. The moisture content at the bottom may be 140% of that at the top of the bed.

2.5e Microbial Community

Ammonia oxidizing bacteria are generally concentrated in the initial portion of the media bed, while densities of nitrite oxidizers are typically homogenous throughout the media (Nijhof and Klapwijk, 1995; Kinney et al., 1998). Studies also indicate that ammonia oxidizers grow faster at start-up, while nitrite oxidizers require a longer growth period to establish steady-state performance (Nijhof and Klapwijk, 1998; Villaverde et al., 1997a). Still, the maximum specific growth rate for nitrifying bacteria is relatively slow because of the low yield of energy from the oxidation of the inorganic energy sources (ammonia and nitirte). A doubling time of eight hours

is possible under ideal conditions (Hagopian and Riley, 1998). Typical in situ doubling times for ammonia oxidizers is 26 hours and 60 hours for nitrite oxidizers (Hagopian and Riley, 1998).

Two parallel studies by Chung et al. (1997, 1998) compared the advantages of a microbial community dominated by a heterotrophic *Arthrobacter oxydans* CH8 to the typical autotrophic *Nitrosomonas europaea* in treating gaseous ammonia. Under typical operating conditions the autotrophic nitrifying bacteria were favorable, however heterotrophic nitrifying bacteria were superior under conditions of acidic pH, high ammonia concentration, and high temperature (Chung and Huang, 1998). While the data indicated that the heterotrophs have a specific nitrification rate up to 10^4 times slower than autotrophs, their biomass concentrations were as much as 10^5 times greater (Chung et al., 1997). The greater biomass concentration can offset the slower specific nitrification rate, but may pose greater problems in biomass accumulation and bed plugging.

The filters in the Chung et al. (1997, 1998) studies were inoculated with pure cultures of their respective nitrifying bacteria and both exhibited removal efficiencies of greater than 95% within 24 hours. The filter inoculated with *N. europaea* initially achieved a higher removal efficiency in less time, 99% in four days compared to 98% in seven days for the *A. oxydans* filter. However, the *N. europaea* filter was subject to repetitive declines in performance over a 12 to 15 day period, requiring the replacement of the growth medium.

The effect of an increased flow rate on the two systems was observed with a constant influent ammonia concentration of 60 ppm_v. Both systems maintained removal efficiencies above 85% with an EBCT above 17 s (*N. europaea* > 90%). Removal efficiencies dropped off significantly at EBCT of 12 s. Both systems demonstrated that the majority (approximately 97%) of the ammonia removal occurred in the first half of the bed with a flow rate below 6100 $m^3/m^3 \cdot d$ (Chung and et al., 1997, 1998). The *N. europaea* filter also experienced lower removal efficiencies from the growth of heterotrophic bacteria (Chung and Huang, 1998).

3. METHODS

3.1 Experimental Design

3.1a General Approach

The intent of this study was to investigate the potential use of a biotrickling filter to remove ammonia from air. Ammonia concentrations relevant to the treatment of waste gas emissions from intensive livestock operations were evaluated, as they examine possible applications in North Carolina. The relevant gas-phase NH_3 concentrations were computed based on an equilibrium with expected liquid-phase concentrations typical of these operations.

Ammonia concentrations in swine waste and the subsequent emissions vary over a large range depending on the form of the waste, as shown in Table 5. Fresh manure and urine contain relatively high concentrations of ammonia, while dewatered manure in the barn sub-floor pits has the highest concentration. Liquid slurry, primarily composed of only the manure and urine, may have ammonia concentrations up to three times higher than the diluted waste flushed to the lagoons from the confinement houses. Settled lagoon water is further reduced in concentration compared to mixed wastes. Throughout the process of collection, transfer, settling, and storage, ammonia nitrogen content decreases through volatilization. Ammonia concentrations in fresh manure fluctuate depending on diet, water intake, feeding methods, and housing facilities. Ambient temperatures, rainfall, dilution by flushing, liquid recycle systems, lagoon dimensions, and mean retention time further influence lagoon ammonia concentrations. A liquid-phase total nitrogen concentration in the range of 1000-2000 mg/L was selected for this project, based on the values reported for the more concentrated forms of hog waste.

Table 5. Typical Nitrogen Content in Various Forms of Swine Waste

Manure Type	Total Nitrogen (N_T)		Ammonium (NH_4-N)		Ammonia (NH_3-N)	
	ppm_v	mg/L	ppm_v	mg/L	ppm_v	mg/L
Fresh[1]	6000		3500			
Liquid Slurry[1,2]		3715		2276		
Anaerobic Lagoon Sludge[1]		2636		719		
Settled Flushed Manure[3]	548					310
Liquid Slurry[4]	3175				2008	
Anaerobic Lagoon Sludge[4]	2926				711	
Anaerobic Lagoon Liquid[4]	563				456	
Barn Sub-Floor Pit (mixed)[5]		7000				3600
Barn Sub Floor Pit (supernate)[5]		5400				3200
Barn Sub-Floor Pit[6]	78000[7]			10,000	39000[7]	
Anaerobic Lagoon Liquid[6]	500-1500		400-1300	460-900	474	300-1000

1. NCSU, CES, 1998, abridged from North Carolina Agricultural Chemical Manual
2. 12 to 6 months accumulation of manure, urine and excess water usage; does not include fresh water for flushing
3. Westerman et al., 1998
4. Barker and Zublena, 1995
5. Chescheir et al., 1986
6. Martin, 1999
7. Total solids basis

The bench-scale biotrickling filter used in this study was designed and operated for potential full-scale implementation. Thus, the results were expected to effectively predict full-scale performance with ammonia as the principal contaminant in an air stream. The trickling filter was constructed as two columns in series and was packed with a patented expanded-clay medium (Infilco-Degremont Biolite™). The two-column design of the biotrickling filter facilitated mid-bed sampling for better performance analyses. The full-bed design height was one meter, and was divided equally between the two columns. The two-column design also allowed for operational flexibility during sampling and maintenance. At full-scale, such a design could provide the ability to switch the series order, which may reduce the need for maintenance and backwashing.

The seed culture of nitrifying bacteria used to inoculate the media bed was developed by enrichment of a sample of activated sludge from a local wastewater treatment plant. After inoculation, air contaminated with a selected ammonia concentration was passed through the columns for treatment. The NH_3 was artificially introduced to the air stream by bubbling the air through an ammonium hydroxide solution. The concentration of ammonia in this solution was adequately maintained with the addition of concentrated ammonium hydroxide using a syringe pump. The air stream was humidified up-stream of the ammonia addition flask by bubbling the air through water, which helped maintain the moisture content within the media.

In addition to the contaminated air, the columns received supplemental water pumped to the head of each column. The water flowed down through the columns by gravity, concurrent with the forced air. The water served three primary purposes. First, the supplemental water ensured adequate moisture content and temperature control within the columns. The influent air was not heated, so condensation within the columns due to cooling was unreliable. Second, the water was buffered with stoichiometrically balanced concentrations of sodium bicarbonate to maintain the pH within the optimum range for the nitrifying bacteria. Third, the water served as the system discharge by removing the nitrite and nitrate produced by the microbes via the liquid effluent. In addition, the water could remove excess biomass from the media and enhance biomass distribution throughout the columns.

A nominal empty bed contact time (EBCT) of 30 seconds was initially selected to determine the reactor performance. This value is consistent with typical biofilter operating conditions (15-60s) used for waste gas treatment (Devinney et al., 1999). The selected EBCT and bed volume resulted in the initial target airflow of 4.0 L/min.

The pK_a for NH_4^+, the dimensionless Henry's coefficient for NH_3, and a pH of 8.5 were used to estimate the gas-phase concentration of NH_3 in equilibrium along with the assumed liquid-phase total nitrogen concentrations of 1000-2000 mg/L in swine waste. The pH of 8.5 is higher than that of raw liquid waste but is consistent with values reported for lagoon wastewater

(Kirchmann, 1994; Martin, 1998). The resultant gas-phase ammonia concentration of 0.197 g NH_3-N/m^3 (0.197 mg/L), corresponding to 2000 mg/L total nitrogen, represents near-worst-case conditions for air emissions from swine waste storage facilities. The calculations at this higher total nitrogen concentration are presented in Appendix A. The gas-phase ammonia concentrations, combined with the design EBCT, defined a target range of loading rates between 0.28 and 0.57 kg N/m^3·d (280 to 570 mg N/L·d).

The biotrickling filter was subjected to three operational conditions, identified as Periods 1 through 3. The lower NH_3-N loading and longer EBCT were selected for Period 1 to assess the initial performance of the biotrickling filter. The influent air stream ammonia concentration and nitrogen loading were doubled for Period 2. With the nitrogen loading remaining the same, the air flow rate was doubled for Period 3, reducing the EBCT and influent ammonia concentration to half of the values from Period 2. Table 6 summarizes the actual operating conditions for the three periods. The averaged mass loads and influent NH_3-N concentrations were based on the daily volumetric addition of NH_4OH solution over each period (sampled and non-sampled days).

Table 6. Average Operating Conditions for Each Period

Period	Dates	Air Flow		EBCT	NH_3-NLoading Rate		Influent NH_3-N (g/m^3)
		(L/min)	(m^3/m^3·min)	(s)	Mass (g/d)	Vol (kg/m^3·d)	
1	Oct 15-25	4.5	2.2	27.1	0.50	0.50 ± 0.10	0.077 ± 0.015
2	Oct 25-Nov 8	4.4	2.2	27.7	0.98	0.98 ± 0.14	0.16 ± 0.029
3	Nov 8-22	8.5	4.2	14.3	1.02	1.02 ± 0.05	0.084 ± 0.009

Based on the assumption that the pH in the ammonia addition flask was much greater than 9.3 (pK_a of ammonium/ammonia), all of the ammonium hydroxide (NH_4OH) added by the syringe pump was assumed to be in the NH_3 form. This assumption of a complete speciation to NH_3 allowed us to equate the amount of ammonia added to the system to the amount of ammonia added to the ammonia-generating flask. Thus, the required quantity of NH_4OH solution was

determined from the nominal NH_3-N mass loads. The concentrated NH_4OH solution has a density of 0.9 g/L and is 30% NH_3 in water.

Nitrification of ammonia (as NH_3) to nitrate consumes a net 3.57 g of alkalinity as $CaCO_3$ / g NH_3-N. When the ammonia (NH_3) in the contaminated air is absorbed into the liquid phase covering the biofilm it is converted to ammonium (NH_4^+). This hydration effectively produces one equivalent of alkalinity in accordance with the equation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \text{ (one equivalent of alkalinity).}$$

The subsequent conversion of ammonium to nitrite (NO_2^-) consumes two equivalents of alkalinity in accordance with the equation:

$$NH_4^+ + 1.5O_2 \leftrightarrow NO_2^- + H_20 + 2H^+ \text{ (two equivalents of alkalinity).}$$

Alkalinity is not consumed during the oxidation of nitrite to nitrate. Using the highest nominal mass loading of 1.15 g NH_3-N/day and the alkalinity consumption of 3.57 g $CaCO_3$/ g NH_3-N, the alkalinity load was calculated to equal 4.07 g $CaCO_3$/day, which corresponds to a sodium bicarbonate ($NaHCO_3$) requirement of 6.8 g/d. The sodium bicarbonate was supplied through the supplementary water at a concentration established to maintain a salt concentration of approximately 2 g/L. The corresponding nominal liquid flow rate was 3.6 L/d or 1.8 $m^3/m^3 \cdot d$ per unit bed volume, which is consistent with liquid flow rates reported in literature (Kinney et al., 1998).

3.1b Physical Design

A schematic of the bench-scale biotrickling filter is shown in Figure 3. The Environmental Science and Engineering shop constructed the columns from acrylic tubing with a diameter of 5.1 cm (2 in). Each column was fitted with differential manometers, inlet and outlet

attachments, and air-tight end caps. Each column provided a media height of 0.5 m (1.6 ft) and a cross-sectional area of 20.3 cm^2 (3.14 in^2). The total bed depth of 1 m provided a volume of 2.03 L (0.002 m^3, 0.07 ft^3). A sturdy wire screen served as the media support and permitted free flow of both water and air. The Biolite™ media was obtained from Degremont North America Research and Development (Richmond, VA) and had an approximate diameter of 0.5 cm (0.2 in). The column diameter was selected to be at least ten times the media diameter to minimize wall effects.

The supplemental water was added at the tops of the columns through a port on the side of the acrylic cylinder, using a multi-head peristaltic pump (Buchler Instruments). A short stainless steel tube with a 90 degree elbow trickled the water onto the center of the bed. The water was removed from the center of the cylinder's end caps. Neoprene tubing (Masterflex™, size 14) was used in the peristaltic pump and adjoined 0.18 cm (1/16 in) tygon™ tubing for the supplemental water feed. The effluent water from both columns was gravity driven through 0.95 cm (3/8 in) tygon and polyethylene tubing. Influent and effluent water were fed from and collected in individual carboys, respectively. A one-liter sample bottle was initially used to hold the liquid effluent of Column 1 prior to pumping to Column 2, which simulated the flow of water through a single, continuous column. The sample bottle was later replaced by a three-liter vessel to increase the system's stability. Water sampling locations are denoted on Figure 3 with four blue triangles labeled IC1, EC1 (influent and effluent Column 1), and IC2, EC2 (influent and effluent Column 2). All tubing remained submerged to prevent short-circuiting of air.

The air was fed from a diaphragm pump (Thomas Industries) via 0.95 cm (3/8 in) polyethylene Bev-a-line™ tubing, to a pulse-dampening pressure tank and a rotameter (Cole Parmer) to measure the flow. The polyethylene tubing was used for the entire air train. The rotameter and pulse-dampener are not shown in Figure 3, but were located immediately following the air pump. The purpose of the pulse-dampening tank was to provide a steady air pressure, as opposed to the rapid pulses of air characteristic of a diaphragm pump. The target feed pressure

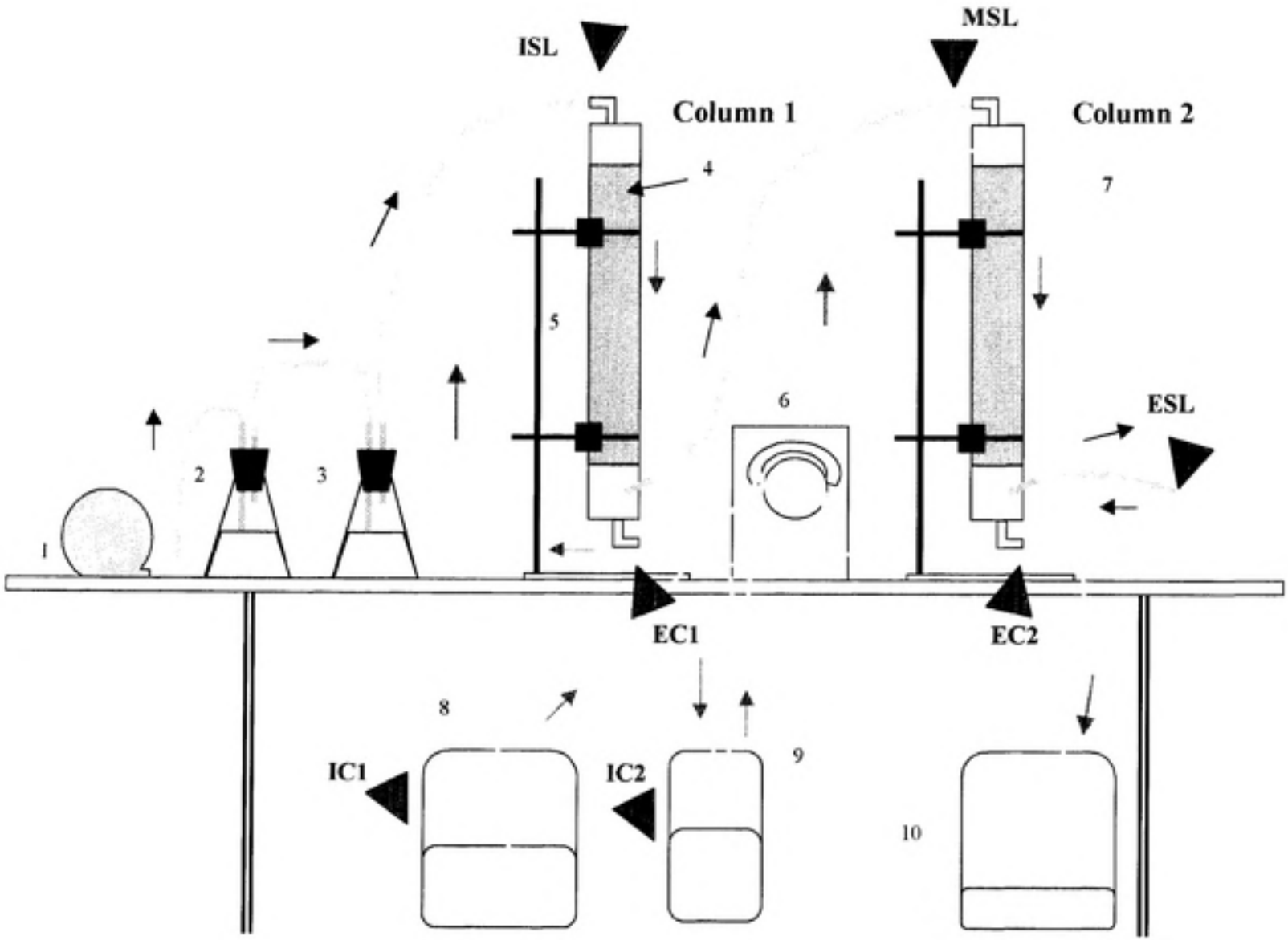


Figure 3. Biotrickling Filter Apparatus
Items are identified in Table 7

Table 7. Identification of Items in Biotrickling Filter Apparatus*

Item	Description
1	Diaphragm air pump
2	Humidification flask
3	Ammonia addition flask
4	Media
5	Ring stand and column supports
6	Peristaltic pump (multi-head)
7	Manometer
8	Feed carboy
9	Intermediate collection vessel
10	Collection carboy
ISL	Influent (gas) sampling location
MSL	Intermediate (gas) sampling location
ESL	Effluent (gas) sampling location
IC1	Column 1 influent (liquid)
EC1	Column 1 effluent (liquid)
IC2	Column 2 influent (liquid)
EC2	Column 2 effluent (liquid)

* Accompanies Figure 3

was 4 psig for Periods 1 and 2. The higher air-flow rate of Period 3 required a feed pressure of 5 psig. Downstream of the rotameter, the air was bubbled through two 2 L air-tight erlenmeyer flasks. The first flask, containing 1.4 - 1.8 L of deionized water, served as a humidifier and the second as the ammonia addition vessel. Concentrated ammonium hydroxide was continuously added to 1.2 - 1.4 L of deionized water in the flask using a syringe pump (Sage Instruments). Both flasks were replenished with deionized water as required. All air tubing was connected to other hardware via compression fittings, allowing quick disconnection and reconnection for sampling.

After adding humidity and ammonia, the air entered the top of Column 1 through the center of the cylinder's air-tight end cap. The exit port was on the side of the acrylic cylinder below the media support. The air subsequently entered and exited Column 2 in the same fashion. The effluent air was discharged via tubing to a laboratory fume hood. Gas-phase samples were collected at the influent, effluent and intermediate (between columns) locations using a gas

washer (Fisher-Milligan). The sampling locations are annotated on the schematic by three red triangles labeled ISL, ESL, and MSL, respectively.

3.2 Biotrickling Filter Operation

3.2a Air Flow Calibrations

Measurements of the air flow rate were calculated from the readings obtained from the rotameter, which was calibrated using a Gilibrator Primary Flow Calibrator. Three sets of rotameter data are included in Appendix B, and are summarized in Figure 4. The calibration dated 6 September was conducted immediately downstream of the rotameter at a source pressure of 3 and 5 psig. A significant conclusion of this calibration was that variations in the pulse dampener pressure setting did not affect the air flow rate.

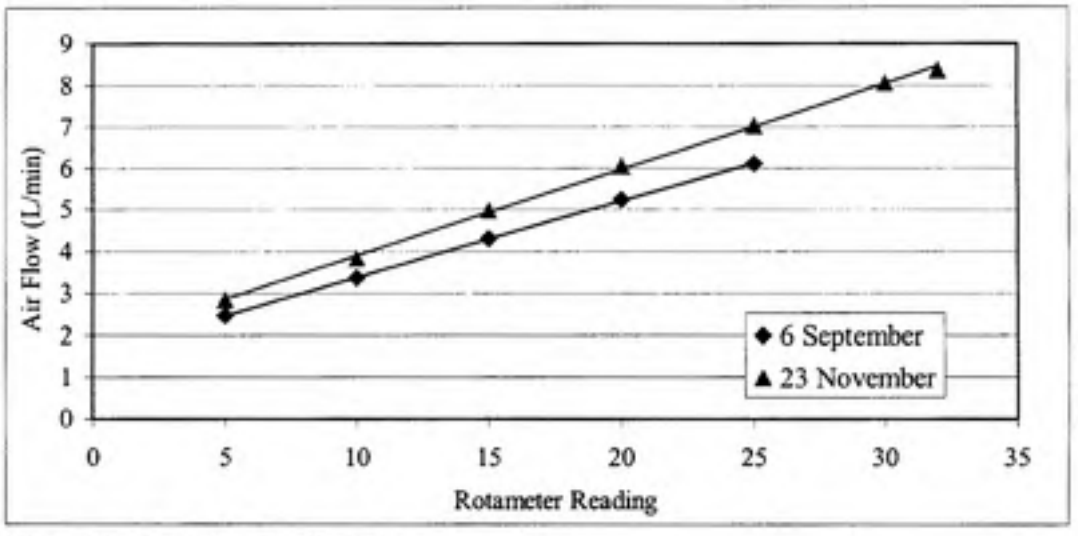


Figure 4. Air Flow Calibrations

The calibration dated 13 November was conducted at the three air sampling locations shown on Figure 3 and immediately downstream of the rotameter. Two rotameter settings and pulse-dampener pressures were selected based on the rotameter settings used during routine

operation of the biotrickling filter. The readings of the first three sampling positions (Column 2 effluent, between columns, Column 1 effluent) for both trials demonstrated that as portions of the system were removed, the air flow remained relatively constant. This confirmed that the air flow was consistent across both columns for the selected operational conditions. The calibration also indicated that the measurements collected at the system effluent more accurately reflected the conditions across the columns than did measurements immediately downstream of the rotameter.

Since only two rotameter readings were used on 13 November, a third calibration was required to fully define the calibration curve. The data from the calibration on 23 November, which was conducted at the effluent of Column 2, are also presented in Figure 4. The resultant equation from this calibration was used for all of the data analyses. The equation is:

$$\textbf{Air flow (L/min)} = 0.2067(\textbf{rotameter reading}) + 1.826. \qquad (5)$$

The straight-line calibration confirmed that the variations in the pulse-dampener pressure setting did not affect the air flow rate, also as concluded in the first calibration. However, comparison of these data to that from 6 September demonstrated a higher air flow rate at the system effluent versus the rotameter effluent for the same rotameter reading (Figure 4). This was due to the fact that the air decreased in pressure and expanded as it passed though the system. This resulted in a higher air flow, since the volume of air increased. This phenomenon was also confirmed by the data obtained during the 13 November calibration, as the rotameter effluent flow rate was lower than the Column 2 effluent flow rate. The rotameter was set to a maximum flow rate or completely open, for the second trial conducted on 23 November. Under this condition, the flow rate was directly a function of the available pressure in the pulse-dampener. The resultant line from this trial was nearly identical to the line described in the equation above. Thus it was concluded that the air flow rate was primarily a function of the rotameter setting, provided that there was enough pressure in the pulse dampening tank to overcome the resistance of the downstream apparatus.

3.2b Seed Culture and Startup

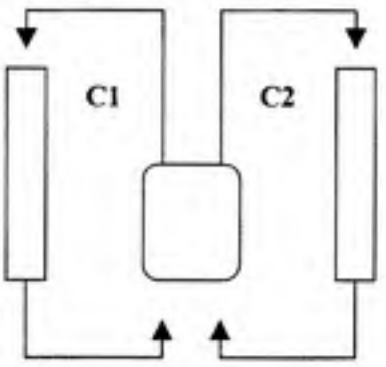
The seed culture was started from a one-liter sample of return activated sludge from the Orange Water and Sewer Authority's Mason Farm Wastewater Treatment Plant, which is operated to perform nitrification. Approximately 750 mL of the sample was added to 15 L of dechlorinated tap water in a 20 L glass carboy, which was mixed with a magnetic stirrer and continuously aerated. The dechlorinated tap water was obtained by aerating the tap water for approximately 2 hours and allowing it to stand for a minimum of 24 hours prior to use. The batch seed culture was enriched by semi-continuous addition of ammonium chloride (NH_4Cl). Sodium bicarbonate ($NaHCO_3$) was added to the culture to provide alkalinity. Over the initial eight-day enrichment period, a total of 1.64 g of NH_3-N and 18.1 g of alkalinity as $CaCO_3$ were added. On two occasions monobasic potassium phosphate (KH_2PO_4) was added to the carboy to ensure adequate amounts of nutrient phosphorus.

Daily pH and periodic alkalinity measurements were conducted on the enrichment culture to maintain a pH range of 7.0 to 8.5. The pH of the seed culture was initially expected to decrease as a result of the release of hydrogen ions associated with nitrification. However, the aeration of the seed culture and the subsequent stripping of CO_2 resulted in a rise in the pH. Dilute hydrochloric acid was added to lower the pH to approximately 7.5 on two occasions when the pH of the seed culture was above 9.0. Reducing the air flow to the carboy mitigated this problem. Salt build-up was minimized by periodically removing 1-2 L of culture through a valve on the bottom of the carboy. In addition to the routine wasting to prevent salt build-up, the seed culture was occasionally settled and the upper third of the volume was decanted and replaced. The volume of the seed culture was maintained at 14 L by replacing lost volume due to wasting and evaporation with dechlorinated tap water or de-ionized water (if dechlorinated tap water was unavailable). Respirometer tests were performed periodically on samples from the carboy to verify biological activity by measuring the oxygen uptake rate after injecting an ammonium

solution in the respirometer vessel. Although specific oxygen uptake rates (rates per unit biomass) were not determined, absolute rates increased throughout the enrichment period.

Operation of the columns began on September 26, 1999. The columns initially received a feed of dechlorinated tap water to wet the media bed. The multi-head peristaltic pump was calibrated during this two-day wetting period. Ten liters of the seed culture were used to inoculate the columns after the 8-day cultivation on September 28, 1999. The flow of air containing the ammonia was started at this time. The remaining seed culture was replenished to 14 L with dechlorinated tap water. The columns were inoculated with the seed culture a second time approximately one week later to help stabilize the columns. To maintain biomass in the columns during startup, the effluent from the columns was collected in a single carboy and recirculated to *both* columns from 28 September until 11 October (Figure 5a). On 11 October the effluent from Column 1 was separately collected and pumped to Column 2 (Figure 5b). The effluent from Column 2 was collected in the feed carboy to provide continuous recirculation of the liquid for the duration of the startup period.

a. 28 September to 11 October



b. 11 Ocotber to 14 October

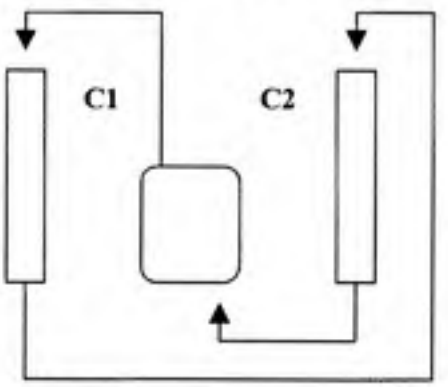


Figure 5. Startup Flow Regimes

Ammonia and nitrate concentrations were measured in the liquid effluents during this period to confirm that nitrification was occurring. Based on the volume of NH_4OH solution

delivered by the syringe pump, an average feed of 480 mg NH_3-N/d was delivered to the system during the startup period. The ammonia feed was increased to an average of 530 mg/d during the period from 11-14 October. By the end of this startup period, there was a visible decrease in the amount of biomass in the liquid effluent from the columns and the headloss rose slightly. These observations, coupled with the confirmation of active nitrification, were strong indicators of a viable nitrifying community. After the 16-day startup period, the system was switched to a continuous operation mode (14 October), in which the effluent from Column 2 was not recirculated. This mode of operation continued through the remainder of the project. For purposes of interpreting performance data presented in Chapter 4, Period 1 began on 14 October, 16 days after start-up (day 0). The first samples were collected on 17 October (day 3).

3.2c Daily Operations

A daily data log was maintained throughout the experiment starting the week of 6 October. The log was revised during the course of the study to incorporate additional information. A copy of the revised data sheet is included in Appendix C. Daily measurements included NH_4OH volume in the syringe; source pressure; rotameter reading; laboratory and column exhaust temperature and humidity; individual column headloss and liquid effluent pH; and container water levels. Liquid-phase ammonia, nitrite, nitrate and total suspended solids (TSS) concentrations, as well as ammonia gas-phase concentrations, were measured periodically. A copy of the sampling schedule for the ammonia, nitrite, nitrate and TSS analyses is also included in Appendix C. Additional samples were collected on occasion depending on the system's performance. The daily data log was completed prior to sampling.

Air and liquid samples were collected across the biotrickling filter starting at the system effluent (Column 2), and systematically working back through the system. This was done to prevent altering conditions by disturbing the system during upstream sampling. Unfortunately, the air flow conditions were adjusted to the design setting prior to sampling, in conjunction with

completion of the daily log. While all subsequent calculations use the corrected flow rate, consistent with the sampling conditions, the sampling conditions do not as precisely reflect the conditions of the system after a day of undisturbed operation. The affect is believed to be negligible with respect to the performance analysis. Performance calculations presented in subsequent tables reflect results from the period *ending* at the time of sample collection.

3.3 Sampling and Analyses

Standard Methods for the Examination of Water and Wastewater (Greenberg et al., 1998) provided background information on all chemical analyses during this study. The analyses included inorganic nitrogen (NH_3-N, NO_2^--N, NO_3^--N), pH, alkalinity, and suspended solids. *Standard Methods* was also consulted for quality assurance, data quality, and sample collection and preservation. Packaged reagents (Hach Company, Loveland, CO) were utilized to simplify the analyses of inorganic nitrogen. A brief description of the inorganic nitrogen analyses utilizing the Hach reagents is included below as they deviate from the procedures presented in *Standard Methods*. The reader is left to consult *Standard Methods* for the description of the other analyses and procedures. A list of the referenced sections is presented in Table 8.

Table 8. Referenced Sections from *Standard Methods for the Examination of Water and Waste Water* (19th Edition)

Analysis	Method and Section	Page[1]
Nitrogen	Method 4500 N	p. 4-75
Nitrogen (Ammonia)	Method 4500 NH_3 A. Introduction B. Preliminary Distillation Step C. Nesslerization Method (Direct)	 p. 4-75/77 p. 4-77/78 p. 4-78/80
Nitrogen (Nitrite)	Method 4500 NO_2- A. Introduction B. Colorimetric Method	 p. 4-83 p. 4-83/84
Nitrogen (Nitrate)	Method 4500 NO_3- A. Introduction E. Cadmium Reduction Method	 p. 4-85 p. 4-87/88
pH Value	Method 4500 H^+ A. Introduction B. Electrometric Method	 p. 4-65 p. 4-65/69
Alkalinity	Method 2320 A. Introduction B. Titration Method	 p. 2-25/26 p. 2-26/28
Solids	Method 2540 A. Introduction D. Total Suspended Solids	 p. 2-53/54 p. 2-56
Quality Assurance	Method 1020 A. Introduction B. Quality Control C. Quality Assessment	 p. 1-4 p. 1-4/7 p. 1-7/8
Data Quality	Method 1030 A. Introduction B. Bias C. Precision D. Total Uncertainty E. Method Detection Level	 p. 1-8 p. 1-9 p. 1-9 p. 1-10 p. 1-10/119
Sample Collection and Preservation	Method 1060 A. Introduction B. Collection of Samples	 p. 1-18/19 p. 1-19-23

1. Page numbers specific to the 19th Edition.

3.3a Ammonia Nitrogen (NH_3-N)

The Hach Nessler Method was used to analyze 25 mL samples in a spectrophotometer (Hitachi U-2000) at a 425 nm wavelength and a 1 cm light path. Nessler Reagent, mineral stabilizer, and polyvinyl alcohol dispersing agent (PDA) were required for this analysis. The mineral stabilizer complexed hardness in the samples, while the PDA aided in the subsequent

color formation. The Nessler Reagent reacted with the ammonium ions to form a yellow complex proportional to the ammonia concentration. The samples did not require preliminary distillation (direct nesslerization) because there were no interfering turbidity or color. The resulting absorbance was used to calculate the concentration of NH_3-N in mg/L from a calibration prepared from standards (NH_4Cl in reagent water) of known concentration. A new calibration was developed for each set of samples. The effective range of this method was 0 to 2.50 mg/L NH_3-N, with an estimated detection limit of 0.1 mg/L NH_3-N. Therefore, some samples required dilutions as high as 100 to 1. Dilutions were performed with volumetric glassware and all samples were analyzed within 30 minutes of collection. Delayed analyses led to decreased concentration of ammonia nitrogen in the samples.

Ammonia analyses were conducted in both water and air samples. Influent water samples were measured to account for background ammonia concentrations, which might result from equilibration with the ambient indoor conditions, as the laboratory was located at a wastewater treatment plant. Water samples collected from the effluent of Columns 1 and 2, and the intermediate collection vessel between the columns, were split for ammonia, nitrite, nitrate and duplicate analyses. Air samples were collected by bubbling the air through 100 mL of a boric acid absorbent (20 g/L H_3BO_3) solution using a Milligan-Fisher gas washer. The duration of the air sample collection was established to ensure an adequate ammonia concentration for analysis. Collection times varied from 50 to 180 minutes for the effluent air samples from Columns 1 and 2, due to the low ammonia concentrations in the air. Although dilution of the influent air samples was routinely required, a sampling period of 6.25 minutes was selected to dampen out concentration fluctuations that might occur in the ammonia addition flask as a result of unsteady delivery of NH_4OH from the syringe pump.

The samples (25 mL) were placed in 40 mL vials for reagent addition. Three drops of mineral stabilizer and PDA were added in that order to each sample. Samples were inverted after each reagent addition to mix. One mL of Nessler Reagent was added to the water samples, and

two mL were added to the boric acid solutions used to absorb the air samples. The additional Nessler Reagent used in the boric acid solutions neutralized their low pH. An alternative method of neutralizing the boric acid with sodium hydroxide prior to analysis produced comparable results.

Five standards of incremental concentrations were prepared from a 1 g/L NH_3-N stock solution. The ammonium stock solution (1.00 g NH_4^+-N/L) was prepared by dissolving 1.91 g of NH_4Cl into 500 mL of deionized water. The stock solution was then diluted 10:1 to produce a 100 mg/L NH_3-N intermediate solution. This intermediate solution was subsequently diluted 33:1, 50:1 and 100:1 to produce 3.0, 2.0 and 1.0 mg/L NH_3-N standards respectively. These standards were additionally used to prepare standards of 0.5, 1.5 and 2.5 mg/L NH_3-N. The 1.5 mg/L NH_3-N standard was prepared by combining 50 mL of the 1 mg/L NH_3-N standard with 50 mL of the 2 mg/L NH_3-N standard. The 0.5 and 2.5 mg/L NH_3-N standards were prepared in the same fashion. All dilutions and composites were mixed using volumetric glassware. Table 9 summarizes the ammonia standards used for the spectrophotometer calibration including the mean and standard deviation of the absorbance values for each standard over the duration of the project.

Table 9. Ammonia Calibration Standards

Name	NH_3-N mg/L	Absorbance	
		Average	Std Dev
Blank (0)*	0.0	0.036	0.003
1	0.5	0.152	0.003
2*	1.0	0.268	0.007
3	1.5	0.375	0.007
4*	2.0	0.502	0.009
5	2.5	0.612	0.009

*Denotes standard used in 3 point calibration

Once procedural confidence was established, only the 0 (deionized water), 1.0 and 2.0 mg/L NH_3-N standards were used to produce the daily calibration curves. At this point 500 ml of the 1.0 and 2.0 mg/L NH_3-N standards were prepared for the duration of the project. The

standards produced linear calibrations with r^2 values ranging from 0.9968 to 1.0. An example of a resultant calibration is presented in Figure 6. Included in Appendix D is a copy of the results from an ammonia analysis spreadsheet used to determine the ammonia concentrations of the respective samples.

Table 1. Calibration Data

Standard NH3 (mg/L)	Absorbance
0.0	0.039
1.0	0.267
2.0	0.503

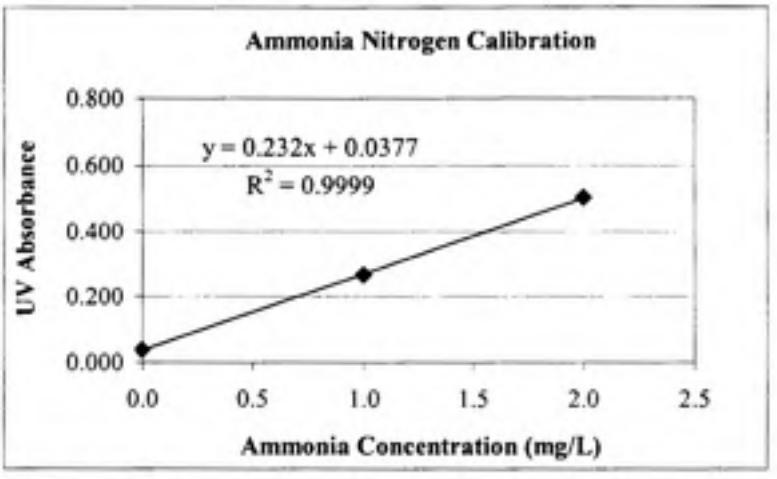


Figure 6. Example Ammonia Nitrogen Calibration

Various dilutions and replicate samples were analyzed with each set of samples to ensure accuracy and reproducibility. Table 10 presents the data from one replicate analysis conducted on the Column 2 liquid effluent. This sample did not require dilution, but the low ammonia concentration was expected to decrease reproducibility as mentioned in *Standard Methods*. The standard deviation of the five analyses of this sample was 4.8% of the mean, demonstrating good reproducibility even at low NH_4^+-N concentrations.

Table 10. Reproducibility of Ammonia Analysis on a Single Sample

Description	Absorbance	NH_3-N mg/L
Aliquot 1	0.091	0.23
Aliquot 2	0.091	0.23
Aliquot 3	0.087	0.21
Aliquot 4	0.093	0.24
Aliquot 5	0.091	0.23
Mean	0.091	0.23
Standard Deviation	0.0022	0.011

The largest variance in reproducibility occurred with samples analyzed at various dilutions. The relative standard deviation was as high as 35% on some analyses. However these poor results occurred with dilutions resulting in ammonia concentrations near or below the method detection limit of 0.1 NH_3-N mg/L. The results from samples diluted to a lesser extent were therefore accepted as more representative. Most of the analyses produced much lower standard deviations consistent with those presented in Table 10 (< 5%).

3.3b Nitrite (NO_2^--N)

The Hach high range nitrite, ferrous sulfate method powder pillows (NitriVer 2 Nitrite Reagent) were used to analyze 25 mL samples. The ferrous sulfate, in an acidic medium, reduced the nitrite to nitrous oxide. The nitrous oxide combined with ferrous ions to form a greenish-brown complex proportional to the concentration of nitrite. The resulting absorbance was used to determine the concentration of NO_2^--N in mg/L from a calibration curve. Nitrite analyses were only conducted on the water samples. Fresh standards and new calibration curves were prepared for each set of samples to preclude standard deterioration from the loss of nitrite through chemical or biological reactions. Some analyses required dilution, as the effective range of this test was 0 to 150.0 mg/L NO_2^-. Most samples were analyzed immediately following collection,

although a few were stored at 4°C and analyzed within 24 hours. Prior to analysis, stored samples were warmed to room temperature.

Deionized water was used to dilute all samples as required, and the 25 mL aliquot was placed in a 40 mL vial. A nitrite reagent pillow was added to each sample and allowed to react for 10 minutes. The absorbance was measured in the spectrophotometer at a wavelength of 585 nm and a 1 cm light path with disposable cuvets (Fischer Scientific). Reagent grade sodium nitrite ($NaNO_2$) and deionized water were used to prepare the standard solutions. A three-point calibration was used on a daily basis, with a six-point calibration used periodically to confirm the calibration's linearity. Table 11 summarizes the nitrite standards used for the calibration. Since the nitrite standards were made fresh for each set of samples, the actual concentrations varied slightly from the target concentrations presented in Table 11. Thus, an average and standard deviation are not computed for the individual standards. Instead, all of the calibration data were used to produce the line presented in Figure 7. The resultant calibration was linear over the range of concentrations tested. Appendix D presents a copy of the results from nitrite analysis spreadsheets.

Table 11. Nitrite Calibration Standards

Name	NO_2^--N mg/L
Blank (0)*	0.0
1	7.5
2	37.5
3*	75.0
4	112.5
5*	150.0

*Denotes standard used in 3 point calibration

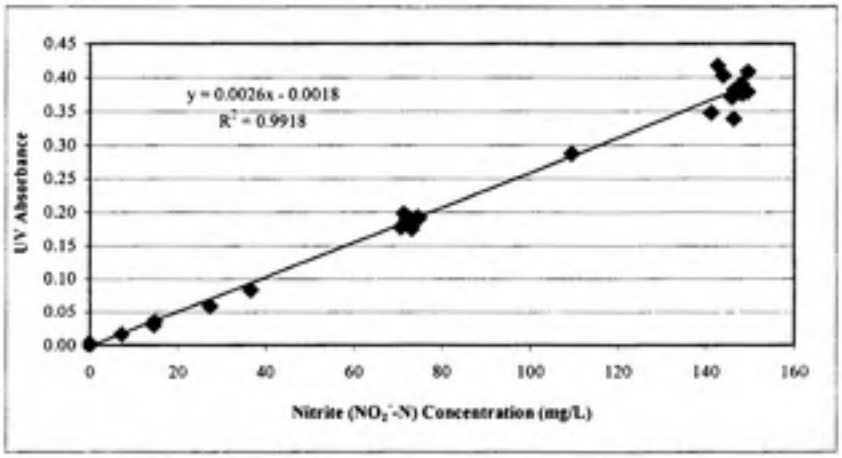


Figure 7. Study Composite Nitrite Calibration

As with ammonia, various dilutions and replicate samples were analyzed with each set of samples to ensure accuracy and reproducibility. Table 12 presents the data from replicate analyses conducted with Column 1 liquid effluent. This sample required a dilution of 10:1 to be within the range of calibration.

Table 12. Reproducibility of Nitrite Analysis on a Single Sample

Description	Absorbance	NO_2^--N mg/L
Aliquot 1	0.155	610
Aliquot 2	0.154	607
Aliquot 3	0.158	622
Aliquot 4	0.155	610
Aliquot 5	0.158	622
Mean	0.156	614
Standard Deviation	0.002	6.0

3.3c Nitrate (NO_3^--N)

The Hach high range nitrate, cadmium reduction method powder pillows (NitraVer 5 Nitrate Reagent) were used to analyze 25 mL samples with a spectrophotometer at a 500 nm

wavelength and a 1 cm light path. The cadmium metal reduced the nitrate to nitrite, which reacts with sulfanilic acid to form an intermediate diazonium salt. This salt coupled with gentisic acid to form an amber-colored azo dye. The resulting absorbance was used to compute the concentration of NO_x^- ($NO_3^- + NO_2^-$) in mg/L from a calibration based on standards prepared from potassium nitrate (KNO_3) solution of known concentrations. A new calibration curve was developed to match each set of analyses. The effective range of this test was 0 to 30.0 mg/L NO_3^--N. The majority of analyses required dilutions, some as high as 100 to 1.

Samples were either analyzed immediately following collection or were preserved with sulfuric acid (pH ~ 2) and stored at 4°C for a period of no more than 14 days. Prior to analysis, preserved samples were warmed to room temperature and neutralized (pH ~ 7) with sodium hydroxide. Again, deionized water was used to dilute all samples as required. The aliquots were placed in 40 mL vials for reagent addition.

Four standards of increasing concentration were prepared from a KNO_3 stock solution (99.9 mg NO_3^--N/L). The stock solution was prepared by diluting 360.3 mg of dried KNO_3 into 500 mL of deionized water. Additional standard solutions were made using the sodium bicarbonate solution that served as the liquid influent to the biofiltration system to determine if any interferences occurred; however, no interferences were observed when these standards were compared to standards prepared with deionized water. Table 13 summarizes the four standards used for calibration.

Table 13. Oxidized Nitrogen (NO_x^--N) Calibration Standards

Name	NO_x-N	Absorbance	
	mg/L	Average	Std Dev
Blank (0)	0.0	0.050	0.006
1	8.0	0.136	0.005
2	16.0	0.190	0.012
3	24.0	0.243	0.110

The standards produced linear calibrations over the range of the analytical method, with r^2 values ranging from 0.981 to 0.989. An example of a resultant calibration is presented in Figure 8. As with ammonia and nitrite, a copy of the results from the analyses is presented in Appendix D. Influent water samples were analyzed on two occasions to quantify background concentrations of nitrate in the dechlorinated tap water. Nitrate was not detected in either sample.

Table 1. Calibration Curve

Standard NOx (mg/L)	Absorbance
0.0	0.046
8.0	0.139
16.0	0.198
24.0	0.251

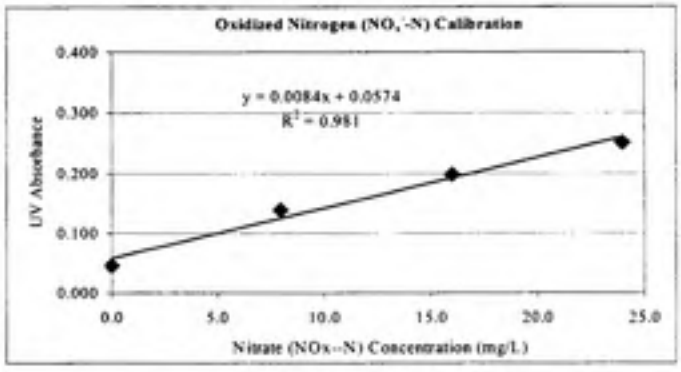


Figure 8. Oxidized Nitrogen (NO_x^--N) Calibration

Various dilutions and replicate samples were analyzed to ensure accuracy and reproducibility. Table 14 presents the data from replicate analyses conducted with a 24 mg/L NO_2^--N standard.

Table 14. NO_x^--N 24 mg/L Standard, Reproducibility

Description	Absorbance
Aliquot 1	0.312
Aliquot 2	0.270
Aliquot 3	0.302
Aliquot 4	0.310
Aliquot 5	0.315
Mean	0.300
Standard Deviation	0.020

3.3d Suspended Solids

The suspended solids analyses were conducted at the end of each of the three operational periods, as indicated on the sampling schedule in Appendix C. The samples were collected from the system effluent (Column 2). A modified procedure from *Standard Methods* was used for the analyses. A glass-fiber filter disk was washed with three successive 20-mL portions of distilled water by vacuum suction and transferred to an inert aluminum weighing dish. The filter was dried in an oven at 103-105°C for approximately 24 hours and cooled in a desiccator prior to weighing. Distilled water was utilized to seat the filter on the apparatus. Two liters of well-mixed effluent sample were then filtered. The filter apparatus was rinsed three times with a 10-mL volume of distilled water, allowing complete drainage between washings. Suction was continued for about 3 min after the visible filtration was complete. The glass filter disk was returned to the same aluminum dish and dried for an additional day at 103 to 105°C. The filter and weighing pan were cooled in a desiccator and weighed as before. The total suspended solids were calculated by the difference in weight divided by the sample volume. Duplicate analyses were completed to verify accuracy.

3.3e Temperature, Humidity, and Alkalinity

The ambient and air stream temperature and humidity were measured using a Temp-Hygro™ pocket probe (Fisher Scientific). The air stream temperature and humidity readings were taken at the system's effluent air flow. The pocket probe's sensor was placed directly in the flow and wrapped with aluminum foil to prevent interference from ambient conditions. Alkalinity was measured through titration of a 200 mL or 100 mL sample with a 0.1 M HCl solution. The titration end-point was selected at the point in the titration curve (pH vs Volume of HCl solution) where the slope (dpH/dV_{HCl}) was the largest.

3.3f Respirometry

The oxygen uptake rate of the nitrifying bacteria was measured using a stirred, water jacketed respirometer cell (Gilson Medical Electronics) and a Clark oxygen electrode (YSI). The test was used to determine the viability of the biomass in the seed culture prior to column inoculation. A 1.7 mL sample of settled mixed liquor from the seed culture vessel was added to the respirometer cell. The cell was aerated to achieve greater than 90% oxygen saturation, then the background oxygen consumption was measured prior to the addition of 10 µL of concentrated (5.7 g/L) NH_4Cl solution. The subsequent oxygen consumption rate was again measured and the net oxygen uptake rate was calculated from the difference between the rates before and after the injection of the NH_4^+.

3.3g Media Adsorption of Ammonia

Since the medium used to pack the biofilter columns was expanded clay, it was of interest to evaluate whether the media could adsorb significant quantities of ammonium. Accordingly, an experiment to determine the potential for ammonia adsorption by the media was conducted in triplicate using a 25 mL volume of unused media. The media samples were submerged in a buffered ammonium solution containing 2.16 g/L $NaHCO_3$ and 0.682 g NH_4Cl/L. The ammonium chloride concentration was proportional to the approximate daily ammonia feed of 500 mg/d scaled down from the bed volume of 2.0 L to the sample volume of 25 ml. The associated calculations are presented in Appendix A. Six 40 mL vials were prepared by adding 25 mL of the buffered ammonium solution. Three of these vials were used as controls (no media) and were subsequently topped off with the ammonium solution to remove headspace. The media samples were added to the 25 mL of solution and slowly agitated by tilting the vials back and forth three times. The samples were agitated to facilitate removal of air pockets, while minimizing volatilization of the ammonia. After allowing the sample to stand for approximately 5 minutes, the vials were topped off with the ammonium solution to eliminate headspace. Table

15 summarizes the preparation quantities. The vials were stored in the laboratory for ten days prior to analysis. A seventh vial was initially prepared with 25 mL of new media and de-ionized water to determine the approximate amount of liquid required to fill the vials. The seventh vial was prepared and stored in a similar fashion.

Table 15. Experimental Parameters for Media Adsorption of Ammonia

Vial	Media		Solution	
	Vol (mL)	Mass (g)	Initial (mL)	Top-off (mL)
Sample 1	25	18.69	25	10.6
Sample 2	25	18.79	25	10.9
Sample 3	25	18.65	25	11.0
Control 1	--	--	25	23.2
Control 2	--	--	25	23.2
Control 3	--	--	25	22.7

3.4 Performance

The results of the gas-phase and liquid-phase ammonia and oxidized nitrogen analyses were used to compute a mass balance on nitrogen over the entire reactor in accordance with the basic premise:

$$\textbf{NH}_3\textbf{-N in (mg N/day)} = \textbf{Inorganic N out (mg N/day)} \qquad (6)$$

where

$$\textbf{Inorganic N out} = \textbf{NH}_3\textbf{-N (gas + liquid)} + \textbf{NO}_2^-\textbf{-N (liquid)} + \textbf{NO}_3^-\textbf{-N (liquid)} \quad (7)$$

Measured concentrations of NO_x^- were converted to mass loads in mg/d for use in the mass balance calculations. Only the NO_x-N concentrations were used in the mass balance computations as they accounted for both the nitrate and nitrite. Thus, the nitrite analyses were not required for the mass balance determination, but were conducted to further define the speciation and the extent of complete nitrification ($NH_3 \rightarrow NO_3^-$).

Calculations of influent NH_3-N loadings obtained from the delivery of the NH_4OH solution were considered to be more accurate than the measurements made on the air grab samples. The mass loads of the respective methods are compared in Figure 9.

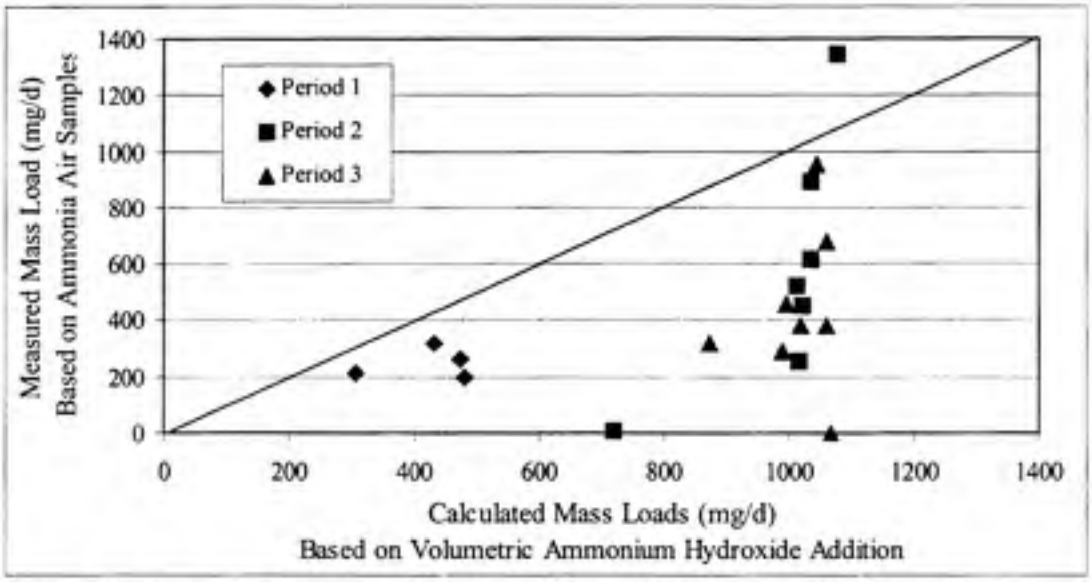


Figure 9. Ammonia Mass Loads, Volumetric vs. Air Sampling Measurements
* The line represents a 1:1 correlation

The mass loads were determined from the measured volumetric change by dividing by the elapsed time in days. Subsequent calculations including the removal efficiency and the nitrogen mass balance used these mass loads.

The low correlation between the methods used to determine the NH_3-N in the influent samples is attributed to the fluctuations in the syringe feed, measurement error, and ammonia trapping inefficiencies in the air samples at the high concentrations in the system influent. The airtight seal and associated friction in the barrel of the syringe caused fluctuations in the delivery of the ammonium hydroxide, which resulted in short-term high or low concentrations of ammonia in the influent air stream. This was evident from the two extremely low and one high mass loads plotted in Figure 9. Thus, the instantaneous measurement of NH_3-N in the air flow was not likely to correlate well with the ammonia delivery integrated over a much longer time period. There is, however, a trend toward underestimating the air concentration of NH_3-N, which was probably

due to trapping inefficiencies. The high air flow rates restricted contact times (<5s), reducing the opportunity to hydrolyze the ammonia. Experiments to evaluate the trapping efficiency for ammonia concentrations consistent with the effluent air stream levels were not conducted. However, it was reasonable to expect that efficiency of the trapping was much higher because of the extremely low concentrations of ammonia in the effluent samples and longer sampling times used. This conclusion was supported by the closer correlation of the mass load measurements obtained with the two methods in Period 1, as shown in Figure 9.

The pulse-dampening tank was unable to sustain the pressure required to maintain the airflow at 9.0 L/min during Period 3. This result was consistent with the final air flow calibration and the corresponding conclusions drawn at the time. While various adjustments, bubble tests and reconnections were unable to identify a particular problem, the most likely cause was a broken seal with the dampening apparatus.

4. RESULTS AND DISCUSSION

The experimental data and calculations are compiled in Tables F1 through F3, Appendix F. The nitrogen species mass loads and concentrations for Column 1 and 2 are summarized in Table F4 and F7.

4.1 Startup

The enrichment of a nitrifying culture from a sample of nitrifying activated sludge was successful. Respirometer analyses confirmed the enrichment of nitrifying bacteria prior to inoculating the columns, as shown in Table 16. Use of this seed culture to inoculate the columns was successful, as evidenced by the 99% removal of NH_3-N within day three of inoculation.

Table 16. Seed Culture Oxygen Uptake Rates

Sample Day during Enrichment	Oxygen Uptake Rate (mg/L min)	
	Initial	After NH_4Cl Addition
0 (startup)	0.2	0.2
3	0.7	1.0
6	0.4	1.9
8	0.2	1.6

4.2 Nitrification Efficiency

Contaminant removal from a waste stream is typically expressed as a removal efficiency (RE) and an elimination capacity (EC). RE is the fraction of the original contaminant removed by the treatment, expressed as a percentage. The RE for this experiment was calculated by:

$$RE = \frac{NH_3\text{-}N_{in} - NH_3\text{-}N_{out}}{NH_3\text{-}N_{in}} \times 100 \quad (\%)$$

The ammonia mass loads (mg/d) in the air and water combined were utilized in this calculation. The elimination capacity (EC) is the mass of contaminant removed or converted per unit volume of the media bed, per unit time. The EC for this study was calculated by:

$$EC = \frac{NH_3\text{-}N_{in} - NH_3\text{-}N_{out}}{V_{bed}} \text{ (mg/L·d) or (kg/m}^3\text{·d)}$$

4.2a Ammonia Removal

The removal efficiencies for Columns 1 and 2, and the biotrickling filter as a whole were calculated from the sampling data. The analyses of the system's influent water confirmed that the ammonia concentration was negligible. The RE for Column 1 is compared to that for the entire system in Figure 10. The majority of the ammonia was removed in Column 1, maintaining a RE of greater than 80% throughout the experiment.

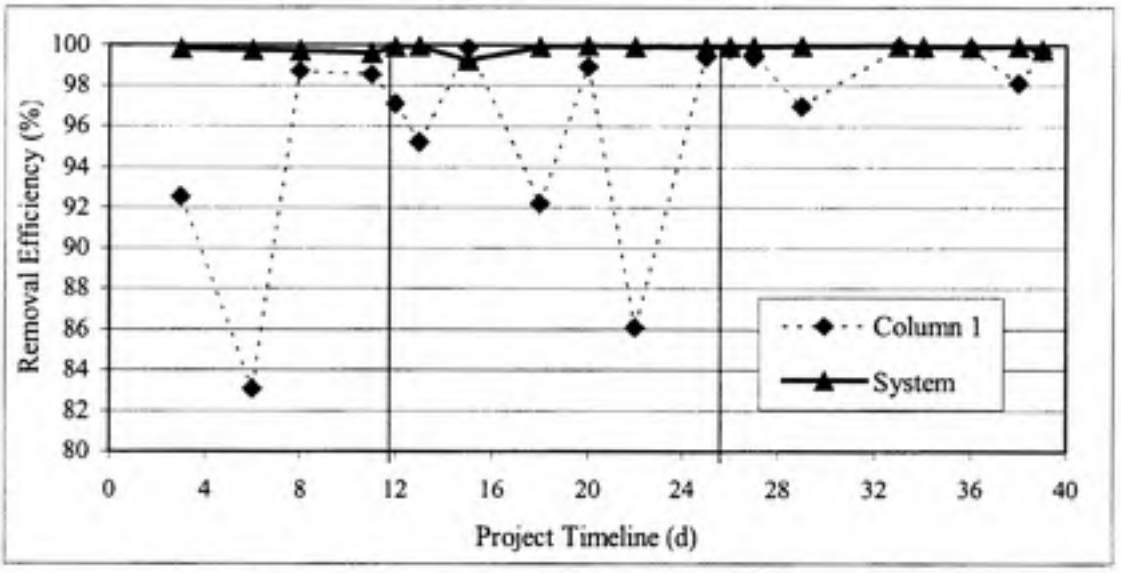


Figure 10. Ammonia Removal Efficiency for Column 1 and the Entire Biotrickling Filter
Vertical lines distinguish the three operating periods. Period 1 began 14 October.

As is evident from Figure 10, Column 2 effectively removed the remaining ammonia to sustain a system RE of greater than 99% for all three operating conditions. The EC of Column 1 is compared to the volumetric load of the system in Figure 11, which also illustrates excellent removal of ammonia in Column 1. Further, Figure 11 demonstrates that the EC of the half- meter deep bed of Column 1 matched the ammonia loading rate with relative consistency. The mean and standard deviation of the volumetric load and EC, along with the removal efficiencies for each period, are listed in Table 17. Since both the loading and EC are based on the effective bed volume, the values listed for Column 1 in Table 17 are approximately twice as large as those listed for the entire system. The resultant loads and ECs for Column 2 were also determined with half of the full media bed.

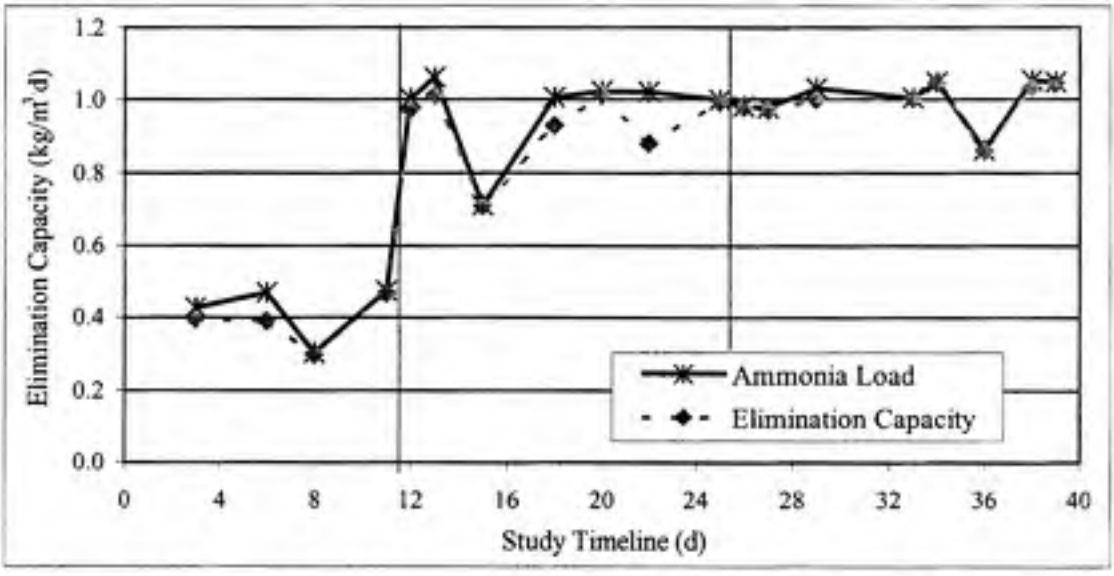


Figure 11. Column 1 NH_3-N Elimination Capacity (kg/m^{3}d) vs. System NH_3-N Load
Vertical lines distinguish the three operating periods. Period 1 began 14 October

The high standard deviation relative to the mean volumetric load in Column 2 (Table 17) resulted from the variability of the ammonia volumetric loads introduced. The variability was directly related to the performance of Column 1. The RE of Column 2 is overlain on the RE of Column 1 in Figure 12. The performance of Column 2 improved with an increased loading, a consequence of lower performance of Column 1. Quantitatively, the RE of Column 2 dropped

below 73% for ammonia loading rates of less than 0.004 kg N/m^3 d. The mean RE increased over the duration of the project. However, due to the extremely high level of efficiency throughout the project, this increase is not viewed as significant or conclusive of better performance.

Table 17. NH_3 Elimination Capacities for Columns 1 and 2, and the Entire System

	Column 1		Column 2		System		
	Loading Rate kg N/m^3 d	Elimination Capacity kg N/m^3 d	Loading Rate kg N/m^3 d	Elimination Capacity kg N/m^3 d	Loading Rate kg N/m^3 d	Elimination Capacity kg N/m^3 d	NH_3 Removal %
Period 1							
Average	0.419	0.388	0.031	0.029	0.209	0.209	99.74
Std Dev	0.079	0.068	0.035	0.035	0.040	0.039	0.09
Period 2							
Average	0.976	0.930	0.046	0.045	0.488	0.487	99.83
Std Dev	0.119	0.109	0.051	0.051	0.059	0.060	0.25
Period 3							
Average	1.002	0.993	0.008	0.008	0.501	0.500	99.94
Std Dev	0.063	0.060	0.011	0.011	0.032	0.032	0.02

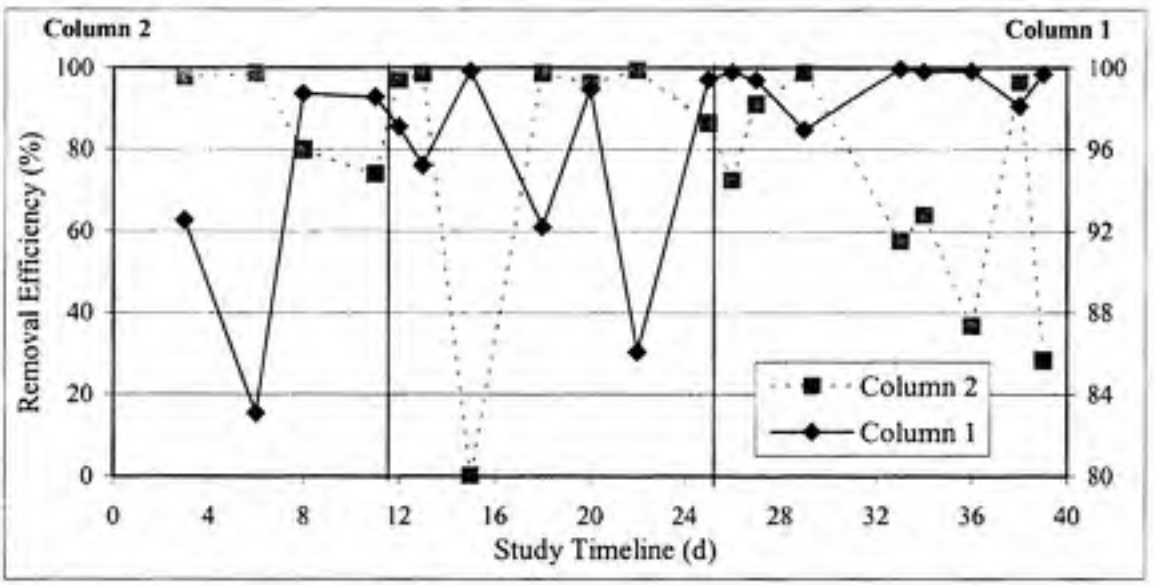


Figure 12. NH_3-N Removal Efficiency for Columns 1 and 2
Vertical lines distinguish the three operating periods. Period 1 began 14 October.

The biotrickling filter's sustained RE of greater than 99%, exceeded previously reported performance of nitrifying biofilters. One comparable study using a gas-phase biotrickling filter reported a removal efficiency of > 98%, for immobilized nitrifying bacteria at a loading rate of

0.10 kg N/m^3·d and an EBCT of 35 s (Chung and Huang, 1998). The removal efficiency decreased to approximately 90% with a reduction in the EBCT to 17 s, which corresponded to a loading rate of 0.21 kg N/m^3·d at the same inlet concentration of 60 ppm$_v$ (Chung and Huang, 1998). The same study calculated a maximum removal rate of 0.40 kg N/m^3·d, which is consistent with biotrickling filter's range in present study of 0.21-0.50 kg N/m^3·d (Table 17). The elimination capacities achieved in the present study can also be compared to the NH_4^+-N removal rates achievable in liquid-waste (wastewater) treatment systems. The removal achieved by Column 1 alone (0.9-1.0 kg N/m^3·d) approached the loading limitations of 1.5 kg N/m^3·d identified by Grady et al. (1999) for a liquid upflow packed bed reactor and 1.1 kg N/m^3·d identified by Villaverde et al. (1997b) for a liquid upflow biological aerated filter. However, Grady et al. (1999), noted significant decreases in removal efficiency above a loading of 1.0 kg N/m^3·d. Similar results were obtained by Villaverde et al. (1997b) with only a 65% removal efficiency achieved at a loading rate of 1.1 kg N/m^3·d.

The gas-phase concentrations of ammonia over the duration of the project are presented in Figure 13. The effluent concentrations from both the entire system (Column 2) and Column 1 alone are well below the acceptable ammonia concentrations and odor levels prescribed by OSHA, NIOSH (US Department of Health and Human Services, 1999) and the American Conference of Governmental Industrial Hygienists (ACGIH) (Schiffman et al., 1995). The concentrations are also better than seven times lower than the levels recommended as reasonable occupational exposure limits (Schiffman, 1998b). Note, a conversion of 1.43 μg NH_3-N/L = 1 ppm$_v$ was estimated for the right Y-axis of Figure 13.

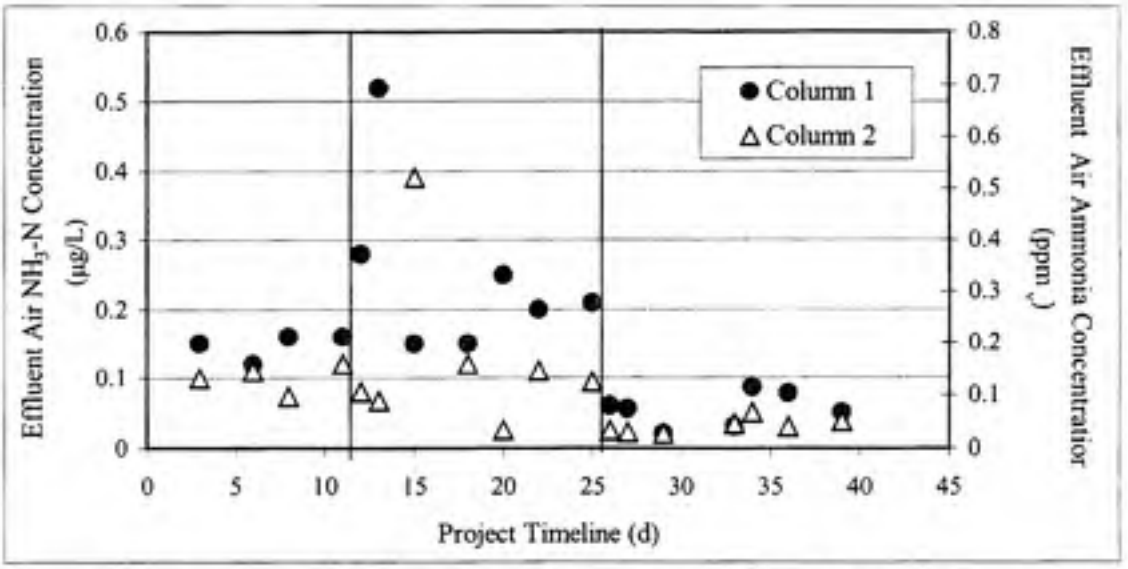


Figure 13. Effluent Air NH_3-N Concentration for Column 1 and the Entire System
The vertical lines distinguish the three operating periods. Period 1 began 14 October.

4.2b Oxidized Nitrogen

The mass loads of oxidized nitrogen in the effluent from each column are plotted in Figures 14 and 15 to illustrate the extent of nitrification in each column. Comparison of the effluent mass loads of NO_2^--N and total NO_x^--N from Columns 1 and 2 suggests that the complete conversion of NH_3 to NO_3^- generally required the entire media bed. Nitrate concentrations were gauged by the resultant difference between the NO_2^--N and total NO_x^--N measurements. While the majority of the ammonia oxidation was completed in Column 1, concentrations of nitrite varied significantly in its effluent as shown in Figure 16. Any remaining ammonia and nitrite were generally removed in Column 2 (Figures 10 and 16). In general, the total NO_x^--N concentration in the effluent from Column 2 was consistent with that in the effluent of Column 1 (Figure 17). However, on a number of occasions the NO_x^--N concentration from Column 2 was lower than that from Column 1. This may indicate a loss of nitrite and/or nitrate via denitrification in Column 2 or the intermediate collection vessel between the columns. This possibility is discussed further below.

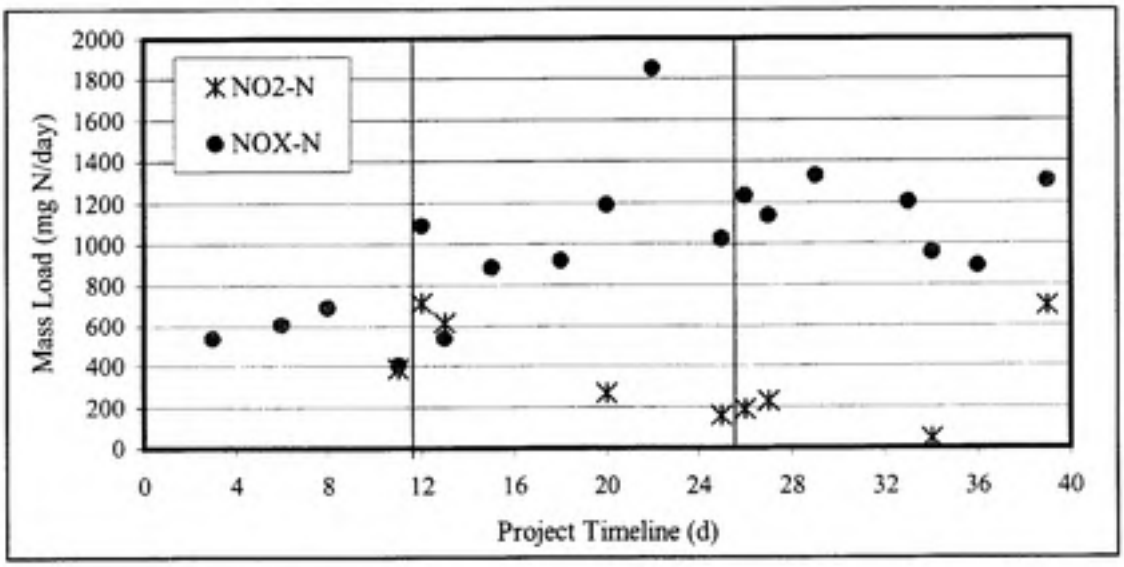


Figure 14. Column 1 Effluent Oxidized Nitrogen Species
The vertical lines distinguish the three operating periods. Period 1 began 14 October.

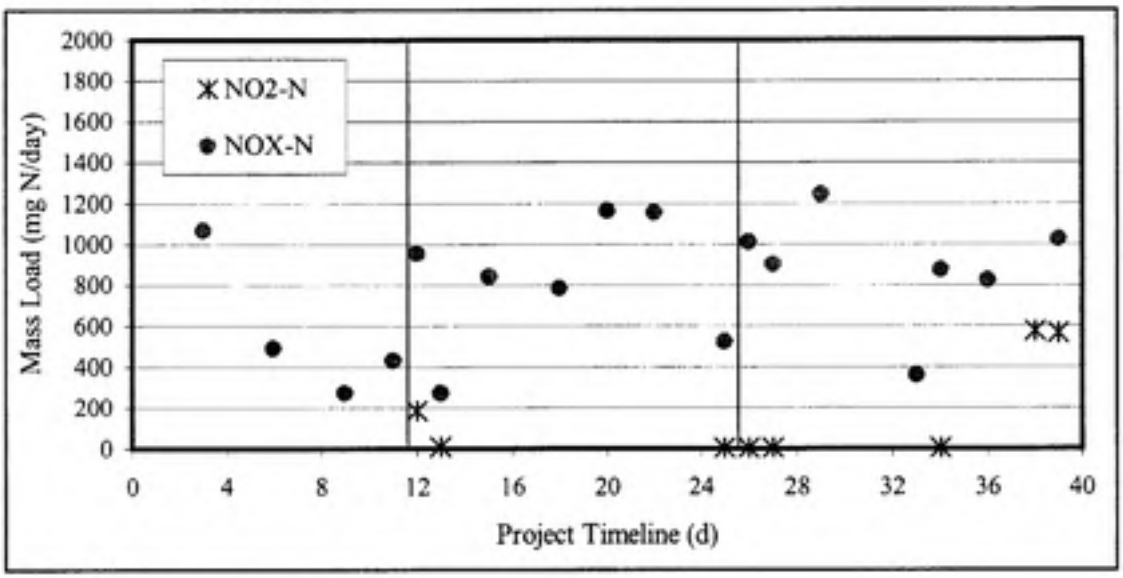


Figure 15. Column 2 Effluent Oxidized Nitrogen Species
The vertical lines distinguish the three operating periods. Period 1 began 14 October

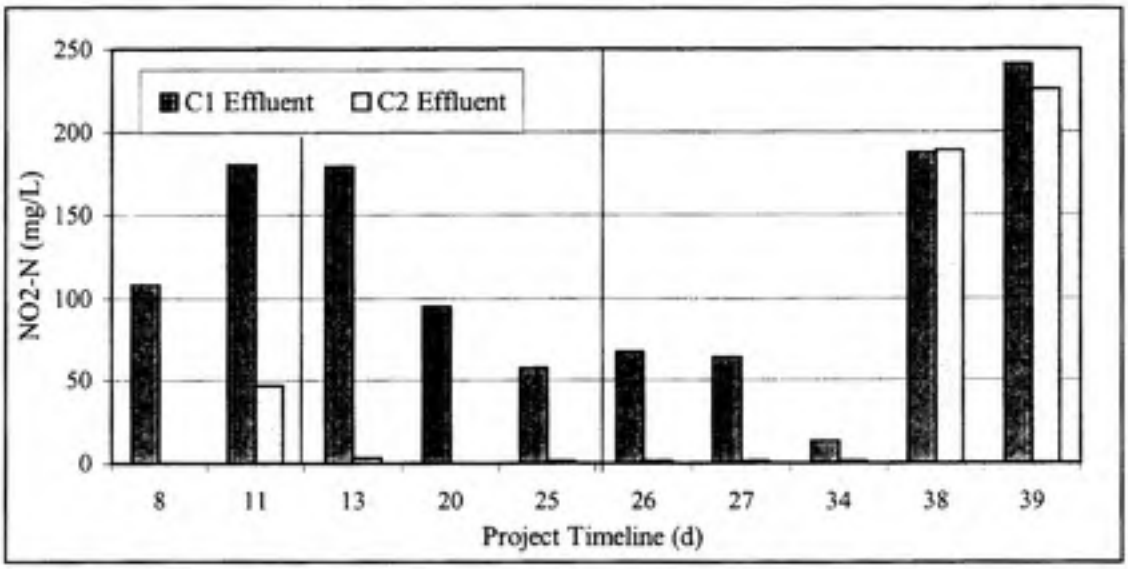


Figure 16. Effluent NO_2^--N Concentrations from Columns 1 and 2
The vertical lines distinguish the three operating periods. Period 1 began 14 October.

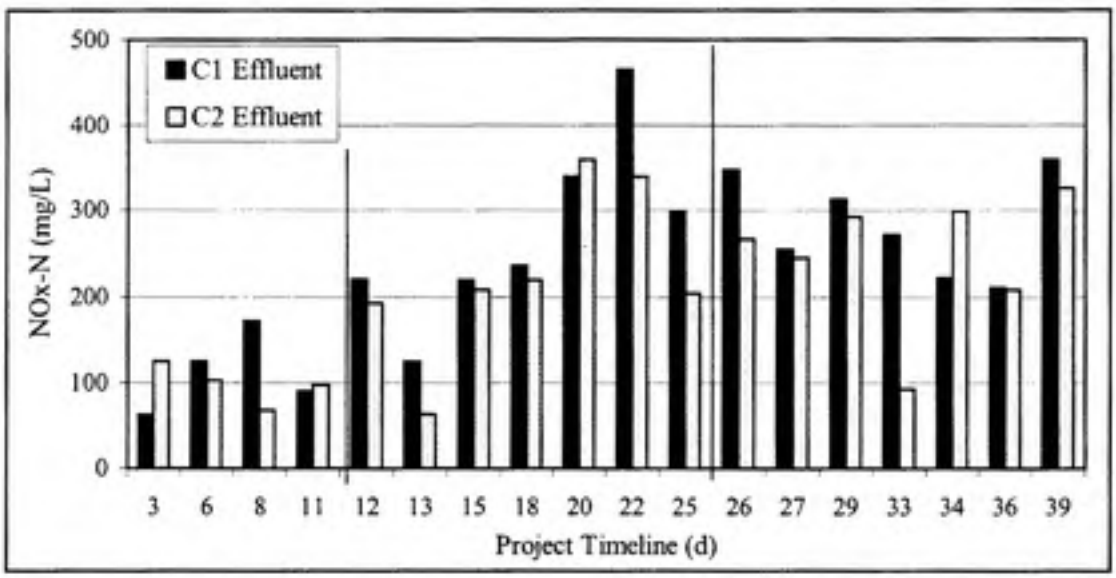


Figure 17. Effluent NO_x^--N Concentrations from Columns 1 and 2
The vertical lines distinguish the three operating periods. Period 1 began 14 October.

The only departure from the trend of complete nitrification from NH_3 to NO_3^- occurred when the biotrickling filter received a sudden increase in the ammonia loading rate. The increase in the mass loading from 0.25 kg/m^3·d to 0.50 kg/m^3·d, during the transition from Period 1 to 2,

resulted in a significant increase in the nitrite concentration from both columns (26 October, Figure 16). The initial lag of nitrite oxidation in both columns was likely due to an insufficient concentration of nitrite oxidizers throughout the system. The microbial community quickly adjusted to the new nitrogen load, as indicated by the decreasing nitrite concentrations in the effluent from both columns in Figure 16. By the end of Period 2, the nitrite concentrations in Column 2 were consistently negligible and the level in Column 1 dropped over 60% from that at the start of the period. The nitrite oxidizing capacity of Column 1 improved approximately four-fold from the first sampling, considering the ammonia mass loading was doubled for Period 2.

The reduction of the EBCT from 28 to 14 s (at the same NH_3-N loading rate) at the beginning of Period 3 did not significantly affect the effluent nitrite concentrations in either column. The effluent nitrite concentrations in Column 1 continued to drop over Period 3 prior to a sudden (accidental) increase in the ammonia load on 20 November. The improved nitrite oxidation capacity resulted in a 93% reduction in the Column 1 effluent concentration from the start of Period 2.

The level of nitrite in the effluent from Column 1 on 21 and 22 November, following the sudden increase in ammonia loading, verified that ammonia oxidation continued despite the high influent concentration. In fact, the ammonia removal efficiency in Column 1 was over 95% within 24 hours of the increased loading. While the residual ammonia from Column 1 was removed in Column 2 in response to this short-term increase, there was no net reduction in nitrite concentration across Column 2. Unfortunately this period coincided with the end of the project, so the longer term response of the nitrite oxidizing community to this sudden increase in the ammonia loading rate is unknown.

Overall, the biotrickling filter was surprisingly resilient during transient conditions. In addition to the accidental increase in loading, two episodes of starvation conditions also occurred on 29 October and 15 November. On both occasions the ammonia feed ceased for approximately

16 hours. The columns did not demonstrate any lag in performance after the ammonia feed was restored.

4.3 Nitrogen Mass Balance

A mass balance on total nitrogen was conducted using the individual species data. The daily mass loads from the gas and liquid phases for the ammonia and the oxidized nitrogen species were totaled for each sampling location. The nitrogen mass balance data for each of the three operational conditions are summarized in Table 18. The influent mass loading of NH_3-N is considered the most accurate of the nitrogen species loading data, as it is based on a daily delivery of ammonium hydroxide to the ammonia-generating flask. In order to compare influent and effluent N directly, the influent data were only evaluated on the days for which total NO_x^--N was measured.

Table 18. Nitrogen Mass Balance Data (mean and standard deviation)

Period	Number of Data Pts	Influent C1 mg N/d	Effluent C1 mg N/d	Effluent C1 p value[1]	Effluent C2 mg N/d	Effluent C2 p value[1]
1	4	423 ± 80	493 ± 82	0.13	455 ± 277	0.37
2	7	988 ± 121	929 ± 324	0.32	725 ± 260	0.015
3	7	1007 ± 65	927 ± 139	0.095	714 ± 217	0.003

1. From two-sided t-test in comparison with influent data

The data indicated that there were no statistically significant differences in the calculated daily mass loads of nitrogen across Column 1 ($p > 0.05$ for all three operating periods). There were however, significantly lower concentrations of total N across the entire system during Periods 2 and 3. This fact is presented graphically in Figure 18 and is consistent with the data on NO_x^--N concentration discussed above. This indicates that some modest nitrogen losses occurred between the effluent of Column 1 and the effluent of Column 2. The open nature of the liquid collection vessel between the columns allowed for some volatilization or oxidation of ammonia prior to entrance to Column 2. A loss of ammonia was confirmed by the lower ammonia

concentrations measured in samples from the intermediate vessel vs. samples collected directly from the liquid effluent of Column 1. Still, this loss was negligible for most daily analyses due to the high removal of ammonia in Column 1. The majority of the system's nitrogen loss was then attributed to the oxidized nitrogen species. This conclusion is consistent with the decrease in oxidized nitrogen concentrations in the effluent of Column 2 relative to Column 1 as shown in Figure 17. The potential for nitrogen losses via volatilization of nitrogen oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), and nitrogen (N_2) existed both in the intermediate vessel and Column 2. Since the gaseous nitrogen species were not sampled for in the effluent air, losses due to the creation of these airborne species throughout the system could not be ascertained.

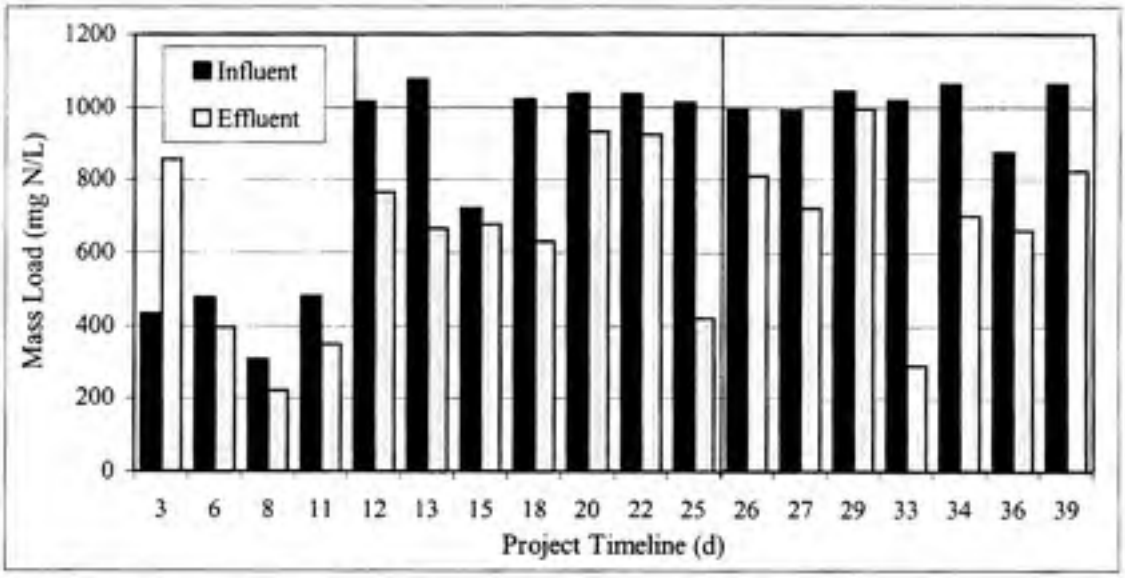


Figure 18. Nitrogen Mass Load, Biotrickling Filter Influent vs. Effluent
The vertical lines distinguish the three operating periods. Period 1 began 14 October.

The potential for denitrification within the biotrickling filter was possible on a microscopic scale. While the majority of the system should have been aerobic, small pockets of oxygen-deficient conditions were likely. Within these anoxic zones in the media bed, the available nitrate and nitrite could have been utilized as electron acceptors for the endogenous respiration of biomass or the oxidation of soluble microbial products. Column 2 was more likely

to support a significant population of denitrifying bacteria. The complete conversion of ammonia to nitrate, which is the preferred electron acceptor, was generally accomplished in Column 2 (initially) or the lower part of the latter half of Column 1 (assuming that ammonia oxidation occurred primarily in the upper part of Column 1).

Nitrogen consumption through microbial growth and adsorption of ammonium ion to the expanded clay media may have accounted for additional losses of nitrogen in the biotrickling filter. Since analyses of the biomass accumulation were beyond the scope of this project, it was not possible to quantify the nitrogen consumption by assimilation. However, low concentrations of effluent suspended solids (Table 19) suggest that the net biomass production in this system was low. Elevated effluent concentrations of ammonia in both the air and water on 29 October, coincident with a loss of ammonia in the influent air, raised the question of possible adsorption-desorption of NH_4^+ in the media. The resilience of the system to the starvation and overload conditions further supported the possible adsorption-desorption of ammonia from the media.

Table 19. Total Suspended Solids Analyses

Period	TSS Duplicates (mg/L)
1	0.9 1.0
2	0.9 0.9
3	1.2 0.9

Two liters of sample filtered through each filter.
Results of duplicate measurements from a single sample.

An experiment was conducted to evaluate the potential sorption of NH_4^+ by the "clean" media. The ammonia analyses and subsequent calculations are included in Appendix E and A, respectively. Unexpectedly, in the equilibrium adsorption tests the media was found to desorb NH_4^+ into solution. Obviously the "clean" media arrived with a substantial amount of sorbed ammonia. Therefore, the media probably desorbed a substantial mass of NH_4^+ during startup and

early in Period 1, as evident by the dramatic increase in nitrogen across the biotrickling filter on 17 October (Figure 18).

The results from the sorption experiment were used to estimate a partitioning coefficient and initial concentration of the ammonia in the media. The partitioning coefficient in deionized water was computed to equal 0.083 mL/g. The initial ammonia concentration in the media was found to equal 0.058 mg NH_3-N/g of media. It is important to note that this ammonia concentration was estimated based on the equilibrium achieved in this one experiment and may not accurately represent the total amount of ammonia initially contained in the media. If the media used in the sorption/desorption experiment was initially saturated with NH_4^+, its sorptive capacity was such that the media in the columns could retain up to 88 g of NH_3-N. This mass is far greater than the daily loading of 0.5 to 1.0 g NH_3-N per day. The ability of the media to desorb and potentially adsorb ammonia probably provided the biotrickling filter the ability to sustain the nitrifying bacteria during the short periods of starvation conditions discussed above, and perhaps the ability to adsorb excess ammonia during periods of high ammonia loading.

4.4 Operational Parameters

Overall, the operational parameters of temperature, humidity, moisture content, headloss, and pH were consistent with the excellent performance of the biotrickling filter, and allowed for direct assessment of the ammonia removal capacity over relatively consistent operational conditions. The mean and range of operational parameters for the three periods and the entire study are presented in Table F8 and F9 Appendix F. The system exhaust and laboratory ambient temperatures were stable throughout the experiment, and were within the range identified as optimum for supporting nitrifying bacteria. The effluent air temperature was consistently cooler than the ambient conditions despite the exothermic metabolic reactions of nitrification. Condensation formed in Column 2 during Period 1, which seems to indicate that greater cooling occurred in the latter portion of the system. This also indicated that the majority of the

exothermic reactions took place in Column 1. The higher energy release expected from the ammonia oxidizers relative to the nitrite oxidizers further supported this reasoning. Any small rise in temperature experienced in Column 1 was expected to boost nitrification, as performance achieves a maximum near 30°C Villaverde et al., 1997a; Hagopian and Riley, 1998; Chung and Huang, 1998).

The stability of the temperature helped sustain the relative humidity within the columns. The estimated average relative humidity of the system exhaust was 88%. On two occasions the measured humidity within the columns dropped below 50% due to mechanical errors. The short-term reductions in humidity did not affect the overall ammonia removal performance of the system. The stability of the system during these conditions was attributed to the sustenance of the liquid film by the addition of the supplemental water. The average liquid flow rate from the feed carboy (3.3 ± 0.4 L/d) was higher than that measured in the effluent collection carboy (2.9 ± 0.5 L/d). The difference was attributed to evaporation from the air flow and exothermic metabolic reactions.

The stability of the headloss measurements across the columns verified a lack of plugging from water or biomass accumulation (Table 20). The slightly higher headloss in Column 1 relative to Column 2 was ascribed to greater biomass density at the influent end of the system, which is consistent with results reported in the literature. The headloss remained relatively constant at 3.9 cm H_2O over the full meter depth of the biofilter during Periods 1 and 2. The doubling of the air flow for Period 3 increased the headloss in both columns, as expected. Previous studies have indicated problems with biomass accumulation, which required the adoption of control techniques. The operation of a column dominated by the relatively low-growth nitrifying bacteria appeared to preclude the development of such problems. This conclusion was supported by low suspended solids concentrations in the system effluent (Table 19).

Table 20. Head Loss and pH for Columns 1 and 2 over the Project Duration
(mean and standard deviation)

	Column 1			Column 2		
	pH Inf	pH Eff	Headloss cm H_2O	pH Inf	pH Eff	Headloss cm H_2O
Period 1						
Mean	**8.41**	**8.12**	**2.2**	**7.79**	**8.26**	**1.7**
Std Deviation	0.12	0.17	0.2	0.20	0.17	0.4
Period 2						
Mean	**8.65**	**8.23**	**2.1**	**8.56**	**8.72**	**1.7**
Std Deviation	0.26	0.42	0.7	0.13	0.17	0.5
Period 3						
Mean	**8.78**	**8.43**	**4.4**	**8.42**	**8.80**	**3.2**
Std Deviation	0.14	0.41	0.5	0.24	0.28	0.3
Study						
Mean	**8.65**	**8.27**	**2.9**	**8.29**	**8.61**	**2.2**
Std Deviation	0.23	0.38	1.2	0.37	0.31	0.8

In general, the pH decreased across Column 1 for the duration of the project as illustrated by the averaged pH measurements listed in Table 20. Such a decrease is consistent with the oxidation of ammonium, which consumes alkalinity, and agrees with the conclusion that the ammonia oxidizing community was concentrated in Column 1. The increase in pH across Column 2 (Table 20) was primarily attributed to the stripping of CO_2 from the supplemental water and suggested the absence of a large ammonia oxidizing community.

5.0 CONCLUSIONS AND RECOMENDATIONS

The biotrickling filter effectively treated the artificially contaminated air stream, sustaining an ammonia removal efficiency of greater than 99% for the duration of the study. The prior enrichment of a culture of nitrifying bacteria and seeding of the columns with the enriched culture achieved this removal within the third day of continuous operation. The entire startup period, including the development of the seed culture and the startup of the biofilter, was completed in less than one month. This short startup period is attributed in part to the rapid biomass retention in the expanded clay medium employed for this project.

The nitrification capacity of the system proved both stable and adaptable. Variations in the influent ammonia concentration, mass loading, and empty bed contact time did not diminish the biotrickling filter's performance with respect to ammonia removal. In addition, small fluctuations in water addition, pH, and temperature experienced during the study did not influence the performance. The headloss across the system remained relatively stable and did not pose a problem. The gradual 50% increase in headloss during Period 3 coincided with an increase in the nitrite oxidation capacity. The supplemental water containing sodium bicarbonate satisfied the alkalinity, inorganic carbon, and other nutrient requirements. The system did not require the addition of phosphorus during the project, which was expected because of the known low net yield of nitrifiers.

The majority of the ammonia entering the biofiltration system was completely oxidized to nitrate. The ammonia and nitrite oxidation steps were relatively isolated in Columns 1 and 2, respectively, during Period 1. Doubling the nitrogen mass load in Period 2 initiated a dramatic, sustained increase in the nitrite oxidation capacity of Column 1, which was extended almost

through the remainder of the study. It was unclear whether the biotrickling filter ever reached steady-state or maximum performance prior to the transient increase in loading at the end of Period 3. The system's stability also increased over the duration of the experiment, including rapid responses to both short-term starvation and sudden increases in loading conditions. The microbial community's ability to consistently oxidize the ammonia, and later the nitrite, at the influent end of the media bed suggested that the biotrickling filter had a greater capacity for ammonia treatment than was utilized in this project. The additional bed volume furnished a comfortable safety factor. Still, caution is warranted for large increases in the nitrogen mass loading because the resulting increase in the liquid-phase ammonium concentration may lead to ammonia inhibition.

The probable development of a limited denitrifying microbial community in Column 2 may have helped to minimize biomass accumulation, which potentially enhances the future implementation of the biotrickling filter as a method of treating ammonia-contaminated air. The initial two-stage performance of the biotrickling filter consisting of ammonia oxidation in Column 1 and nitrite oxidation in Column 2, supports the potential use of a series of columns for the removal of specific contaminants. The high performance of Column 1 further suggests the flexibility of the system to sustain performance during operational restructuring and maintenance. As noted in Chapter 2, such a design can also help to mitigate potential headloss problems by permitting the reordering in the sequence of the columns. The apparent adsorptive-desorptive characteristics of the Biolite^{TM} media contributed to the potential full-scale success of the biofilter by providing the ability to mitigate starvation and possibly overload conditions. Further research is required to better quantify this valuable media characteristic.

In addition to the suggested work with the media, further research into the performance limitations of the biotrickling filter would identify optimum operational conditions. Higher ammonia loads and lower EBCTs would quantify the maximum capacity of the system. The extremely high performance of the filter at all conditions in this study precluded this assessment.

Elevated ammonia concentrations and the introduction of other contaminants, such as volatile organcis, may cause significant competition or inhibition, making this a prominent topic for study. Common gases from agricultural operations include hydrogen sulfide, methane, volatile fatty acids and numerous other organics. The ability of the biotrickling filter to accommodate the synergistic effects of numerous pollutants and adapt to the variations in environmental conditions is paramount to its future employment. Additional proof of the biotrickling filter's relative cost-effectiveness, operational simplicity, and treatment efficiency will define the feasibility of full-scale implementation.

The twenty-first century will witness increases in production and the development of new products to sustain the demands of a society advancing in number and sophistication. This growth is likely to further the stress on the environment and the encroachment of residential areas on industrial operations. The population will require industry to meet consumer demands while fostering a cleaner environment. Industry is expected to respond by utilizing the benefits of economies of scale, as is evident in the swine industry today. This study demonstrates the development potential of biofiltration as one technology capable of satisfying industry's demands for effective large-scale treatment of waste streams, while mitigating the adverse impacts to the health of the environment and society.

REFERENCES

Amirhor, P., Kuter, G.A., and Andrade, M.D. (1995) "Biofilters and Biosolids," Water Environment and Technology, Vol. 7, No. 3, pp. 44-48.

Anderson, B., Aspegren, H., Parker, D., and Lutz, M., "High Rate Nitrifying Trickling Filters," Water Science Technology, Vol. 9, pp. 47-52, 1994.

Aneja, V.P., Chauhan, J.S., and Walker, J.T. (1999) "Characterization of Ammonia Emissions from Swine Lagoons," Draft Report to North Carolina Division of Air Quality.

Aneja, V.P. Murray, G.C., and Southerland, J. (1998) "Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, Deposition, and Assessment," Environmental Manager, The Air and Waste Management Association, pp. 22-25.

Battaye, R., Battaye, W., Overcash, C., and Fudge, S. (1994) "Development and Selection of Ammonia Emission Factors," EPA Contract Number 68-D3-0034, Work Assignment O-3, United States Environmental Protection Agnecy, Research Triangle Park.

Barker, J.C. and Zublena, J.P. (1995) "Livestock Manure Nutrient Assessment in North Carolina," Proceedings, Seventh International Symposium on Agricultural and Food Processing Wastes, Chicago.

Bohn, H.L. and Bohn, K.H. (1999),"Moisture in Biofilters," Environmental Progress, American Institute of Chemical Engineers, Vol. 18, No. 3, pp. 156-161.

Chung, Y.C. and Huang, C.P. (1998) "Biotreatment of Ammonia in Air by an Immobilized *Nitrosomonas europaea* Biofilter," Environmental Progess, Vol. 17, No. 2, pp. 70-76.

Chung, Y.C., Huang, C.P., and Tseng, C.P. (1997) "Biotreatment of Ammonia from Air by an Immobilized *Arthrobacter Oxydans* CH8 Biofilter," Biotechnology Progress, Vol. 13, pp. 794-798.

Cole, D.J., Hill, V.R., Humenik, F.J., and Sobsey, M.D. (1999) "Health, Safety and Environmental Concerns of Farm Animal Waste," Occupational Medicine: State of the Art Reviews, Vol. 14, No. 2.

Devinny, J.S. (May 1999) "Biofiltration for Air Pollution Control," University of Southern California, Environmental Engineering Program, online, Internet, www-rcf.usc.edu/~bfilter /intro.html.

Devinny, J.S., Deshusses, M.A., and Webster, T.S. (1999) Biofiltration for Air Pollution Control, CRC Press, Boca Raton, FL.

Donham, K.J. and Leininger, J.R. (1989) "Animal Studies of Potential Chronic Lung Disease in Swine Confinement Buildings," American Journal of Veterinary Medicine, Vol. 45, p. 926-33.

Duke University, Nicholas School of the Environment (1996) "Policy Recommendations for Management of Agricultural Animal Waste in North Carolina," Report of the Animal

Agricultural Animal Waste Task Force, online, Internet, www.env.duke.edu/faculty/sigmon/agwaste/contents.html.

Fdz-Polanco, F., Villaverde, S., and Garcia, P.A. (1994) "Temperature Effect on Nitrifying Bacteria Activity in Biofilters: Activation and Free Ammonia Inhibition," Water Quality International 1994. Part 11: Biofilm Systems, pp. 121-130, abstract online, Water Resources Abstracts.

Fdz-Polanco, F., Villaverde, S., and Garcia, P.A. (1996) "Nitrite Accumulation in Submerged Biofilters – Combined Effects," Water Science and Technology, Vol. 34, No. 3-4, pp. 371-378.

Grady, C.P.L., Jr., Daigger, G.T., Lim, H.C. (1999) Biological Wastewater Treatment, Marcel Dekker, New York, NY, pp. 3-53, 95-14, 843-899, 964-65.

HACH Company (1997) Water Analysis Handbook, HACH Company, Loveland, CO.

Hagopian, D.S. and Riley, J.G. (1998) "A Closer Look at the Bacteriology of Nitrification," Aquacultural Engineering, Vol. 18, No. 4, pp. 223-244.

Hammond, C. (1994) Animal Waste and the Environment, University of Georgia College of Agricultural and Environmental Sciences, Cooperative Extension Service, Circular 827, online, Internet, www.ces.uga.edu/pubcd/c827-w.html.

Hartung, J. (1992) "Emission and Control of Gases and Odorous Substances from Animal Housing and Manure Depots," Zentralbl-Hyg-Umweltmed, Vol. 192, No. 5, pp. 389-418, OSH-ROM, Medline OEM 1991-1998.

Hinz, T. and Linke, S. (1998) "A Comprehensive Experimental Study of Aerial Pollutants In and Emissions From Livestock Buildings; Part 1, Methods, Journal of Agricultural Engineering Research, Vol. 70, No. 1, pp. 111-118.

Hog Watch (1998) Environmental Impacts of Hog Factories in North Carolina, Environmental Defense Funds, online, www.hogwatch.org/getthefacts/factsheets/enviroimpacts.html.

Honeyman, M.S. (1996) "Sustainability Issues of U.S. Swine Production," Journal of Animal Science, Vol. 74, pp. 1410-17.

Hunt, J.B. Jr, Governor, (1998) Framework for the Conversion of Anaerobic Swine Waste Lagoons and Sprayfields, North Carolina Department of Environment and Natural Resources, online, www.enr.state.nc.us/files/hogs/hogplan.pdf.

Kinney, K.A., Wright, W., Chang, D.P.Y., and Schroeder, E.D. (1998) "Biodegradation of Vapor-Phase Contaminants," Bioremediation: Principles and Practice. Volume I, Fundamentals and Applications, Sikdar, S.K., and Irvine, R.L., ed, Technomic Publishing, Lancaster, pp. 601-632.

Kirchmann, H. (1994) "Animal and Municipal Organic Wastes and Water Quality," Soil Processes and Water Quality, ed. Lal, R. and Stewart, B.A., Lewis Pub., CRC Press, Boca Raton, FL.

Lekang, O.I. and Kleppe, H. (2000) "Efficiency of Nitrification in Trickling Filters Using Different Filter Media," Aquacutural Engineering, Vol. 21, No. 3, pp. 181-199.

Le Tallec, X., Zeghal, S., Vidal, A., (1997) "Effect of Influent Quality Variability on Biofilter Operation," Water Science and Technology, Vol. 36, No. 1, pp. 111-117.

Li, X.W. (1997) "Effects of Dust and Contaminants in Animal Buildings on Human Health," Journal of Environmental Science and Health; Part A, Environmental Science and Engineering, Vol. 32, pp. 2449-69.

McBride, D.A., State Health Director (1998) The Association of Health Effects with Exposure to Odors from Hog Farm Operations, State Health Director, North Carolina Department of Health and Human Services.

McNevin, D., Barford, J., and Hage, J. (1999) "Adsorption and Biological Degradation of Ammonium and Sulfide on Peat," Water Research, Vol. 33, No. 6, pp. 1449-59.

Madigan, M.T., Martinko, J.M., and Parker, J. (1997) Brock Biology of Mircoorganisms, 8th ed., Prentice Hall, Upper Saddle River, pp. 495-529, 571-573.

Marrietta College, Biology Department (1999) "Nitrogen Cycle," Environmental Biology – Ecosystems, online, Internet, www.marietta.edu/~biol/102/ecosystem.html.

Martin, K.J. (1993) "Comments submitted to Rock County Commissioners – May 3, 1999," Martin Environmental Services, Norman, OK. Note: wastewater analysis reports also received in hardcopy.

Michette, T. (1996) "Nitrifying Bacteria and Biofiltration," Philip Barbour High School, online, Internet, www.wvonline.com/pbhs/bio.htm.

Morales, M., Rivah, S, and Auria, R. (1998) "Start-Up and the Effect of Gaseous Ammonia Additions on a Biofilter for the Elimination of Toluene Vapors,' Biotechnology and Bioengineering, Vol. 60, No. 4, pp. 483-91.

Nijhof, M. and Klapwijk, A. (1995) "Diffusional Transport Mechanisms and Biofilm Nitrification Characteristics Influencing Nitrite Levels in Nitrifying Trickling filter Effluents," Water Research, Vol. 29, No. 10, pp. 2287-92.

North Carolina Administrative Code (NCAC) (1998) North Carolina Air Quality Rules, 15A NCAC 2D, Air Pollution Control Requirements, online, Internet, daq.state.nc.us/Rules/ Rules, effective (1 Jul 1998).

North Carolina Board of Science and Technology, The North Carolina Swine Industry, Technology, and Solution to the Problem of Waste and Odor, Raleigh, NC, 1996.

North Carolina Department of Agriculture (NCDA) (Sep 1999) Agricultural Statistics Service, Livestock, Poultry and Dairy – Livestock Page, online, Internet, www.agr.state.nc.us/stats/ livestoc/ livestoc.htm.

North Carolina Department of Environment and Natural Resources (DENR), Division of Air Quality (Feb 1999a) "Controlling Odors from Animal Operations," brochure, (Feb 1999),

online Division of Air Quality Brochures, Internet, daq.state.nc.us/Publications/Brochures. animodor.pdf.

North Carolina Department of Environment and Natural Resources (DENR), Division of Air Quality (Oct 1999b) "EMC Adopts Permanent Animal Odor Control Rules," Division of Air Quality News, online, Internet, daq.state.nc.us/News/101499odor.html.

North Carolina Department of Environment and Natural Resources (DENR), Division of Air Quality (Jun 1999c) "Status Report on Emissions and Deposition of Atmospheric Nitrogen Compounds from Animal Production in North Carolina," online, Internet, daq.state.nc.us/Offices/ Monitoring/Projects/nstatusreport.pdf.

North Carolina Department of Environment and Natural Resources (DENR), Environmental Management Commission (EMC, 1999) "Section .1802 Control of Odors from Animal Operations using Liquid Animal Waste Management System," Division of Air Quality Rules, online, Internet, daq.state.nc.us/Rules/Adopted/PermanentRule.pdf, signed (14 Oct 1999), effective (Jul. 1, 2000).

North Carolina Department of Environment, Health and Natural Resources (DEHNR), Division of Air Quality (1997) "Assessment Plan for Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, and Deposition."

North Carolina General Assembly (1999) "Clean Water Act of 1999," House Bill 1160, online, Internet, www.ncga.state.nc.us/, signed (21 Jul 1999).

North Carolina General Assembly (1998) "An Act to Provide for the Registration of Swine Operation Integrators by Swine Growers," House Bill 1480, online, Internet, www.ncga.nc.us/, signed (20 Oct 1998).

North Carolina General Assembly (1997) Clean Water Responsibility and Environmentally Sound Policy Act," House Bill 515, online, Internet, www.ncga.nc.us/, signed (27 Aug 1997).

North Carolina State University (NCSU) (Jun 1999) College of Agriculture and Life Sciences, Waste Management Program, "Publications and Special Reports: Research Progress Report," online, www.cals. ncsu.edu/waste_mgt/1999report.html.

Nowak, D. (1998) "Health Effects of Airborne Pollutants Particularly in Swine Confinement Houses – A Review Focusing on Aspects of Occupational Medicine," Deutsche Tierarztliche Wochenschrift, Vol. 105, No. 6, pp. 225-34.

Patterson, D. (11 Feb 2000) "State takes first steps to phase out hog lagoons," Associated Press, Raleigh News and Observer, Orange Edition, 3A.

Schiffman, S.S. (1998a) "Complaints of Health Symptoms from Odors Associated with Intensive Livestock Operations," Health and Environment Digest, The Freshwater Foundation, Vol. 12, pp. 60-62.

Schiffman, S.S. (1998b) "Livestock Odors: Implications for Human Health and Well-Being," Journal of Animal Science, Vol. 76, pp. 1343-55.

Schiffman, S.S., Miller, E.A.S., Suggs, M.A., and Graham, B.G. (1995) "The Effects of Environmental Odors Emanating from Commercial Swine Operations on the Mood of Nearby Residents," Brain Research Bulletin, Vol. 37, pp. 369-35.

Schiffman, S.S., Walker, J.M., Small, R, and Millner, P.D. (1998) "Workshop on Health Effects of Odors," Animal Production Systems and the Environment: An International Conference on Odor, Water Quality, Nutrient Management and Socioeconomic Issues, Iowa State University, Des Moines, pp. 407-12.

Shukula, N.P. (1991) "Air Pollution by Odor-Sources," Identification and Control, Reviews on Environmental Health, Vol. 9, No. 4, pp. 239-44.

Smith, K.A. and Frost, J.P. (2000) "Nitrogen Excretion by Farm Livestock with Respect to Land Spreading Requirements and Controlling Nitrogen Losses to Ground and Surface Waters, Part 1: Cattle and Sheep," Bioresource Technology, Vol. 71, pp. 173-81.

Smith, K.A., Charles, D.R., and Moorhouse, D. (2000) "Nitrogen Excretion by Farm Livestock with Respect to Land Spreading Requirements and Controlling Nitrogen Losses to Ground and Surface Waters, Part 2: Pigs and Poultry," Bioresource Technology, Vol. 71, pp. 183-94.

Snoeyink, V.L., and Jenkins, D. (1980) Water Chemistry, Wiley and Sons, New York, NY, pp. 13-14, 90-91, 156-83.

Thomas (1999a) Legislative Information on the Internet, Bill Summary and Status for the 106th Congress, H.R.684, Farm Sustainability and Animal Feedlot Enforcement Act, online, Internet, thomas.loc.gov.

Thomas (1999b) Legislative Information on the Internet, Bill Text, H.R.684, Farm Sustainability and Animal Feedlot Enforcement Act, online, Internet, thomas.loc.gov.

Thu, K., Donham, K.J., Ziegenborn, R., Reynolds, S., Thorne, P.S. (1997) Subramanian, P., Whitten, P., and Stookesberry, J., "A control Study of the Physical and Mental Health of Residents Living Near a Large Scale Swine Operation," Journal of Agricultural Safety and Health, Vol. 3, No. 1, pp. 13-26.

Thu, K. (1998) "Odor Problems from Large-Scale Agriculture: Nuisance or Public Health Problem?" Health & Environment Digest, The Freshwater Foundation, Vol. 12, pp. 57-59.

United States Department of Agriculture (USDA)(Sep 1998) and United States Environmental Protection Agency (USEPA), Draft Unified National Strategy for Animal Feeding Operations, online, Internet, www.epa,gov/cleanwater/afo/.

United States Department of Health and Human Services: CDC & NIOSH (1994) NIOSH Pocket Guide to Chemical Hazards (DHHS/94-116), U.S. Government Printing Office, Washington D.C. Values referenced validated telephonically, February 2000.

United States Environmental Protection Agency (USEPA) (1999) Guidance Manual and Example NPDES Permit for Concentrated Animal Feeding Operations, Review Draft, online, Internet, www.epa,gov/owm/afo.htm#Permit Guidance.

United States Environmental Protection Agency (USEPA) (1998), Office of Wastewater Management and Office of Water, Animal Feeding Operations, AFO, online, Internet, www.epa,gov/owm/ afo.htm#cafo.

Villaverde, S., Fdz-Polanco, F., and Garcia-Encina, P.A. (1997a) "Influence of pH Over Nitrifying Biofilm Activity in Submerged Biofilters," Water Research, Vol. 31, pp. 1180-86.

Villaverde, S., Fernandez, M.T., Uruena, M.A., and Fdz-Polanco, F. (1997b) "Influence of Substrate Concentration on the Growth and Activity of a Nitrifying Biofilm in a Submerged Biofilter," Environmental Technology, Vol. 18, No. 9, pp. 921-28.

Webster, T.S., Cox, H.H.J., and Deshusses, M.A. (1999) "Resolving Operational and Performance Problems Encountered in the Use of a Pilot/Full-Scale Biotrickling Filter Reactor." Environmental Progress, American Institute of Chemical Engineers, Vol. 18, No. 3, pp. 163-72.

Westerman, P.W., Bicudo, J.R., and Kantardjieff, A. (1998) "Aerobic Fixed-Media Biofilter Treatment of Flushed Swine Manure", 1998 ASAE Annual International Meeting, online, www.cals.ncsu.edu/waste_mgt/eko1.htm.

Wing, S. and Wolf, S. (2000) "Intensive Livestock Operations, Health, and Quality of Life among Eastern North Carolina Residents ", Environmental Health Perspectives, Journal of the National Institute of Environmental Health Sciences, Vol. 108, No. 3, pp. 233-38.

APPENDIX A

DESIGN CALCULATIONS:

Total Nitrogen Concentration,
Typical anaerobic lagoon liquid and sludge $[N_T] = 2000$ mg/L

Selected pH
Typical anaerobic lagoon liquid pH = 8.5

Henry's Constant, Ammonia (dimensionless) $K_H^\circ = 7.2 \times 10^{-4}$

Ammonium-Ammonia Equilibrium Constant pKa = 9.3

$$[N_T] = [NH_4^+] + [NH_3]$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \rightarrow \quad -\log K_a = -\log [H^+] - \log \frac{[NH_3]}{[NH_4^+]}$$

$$pKa = pH - \log \frac{[NH_3]}{[NH_4^+]}$$

$$9.3 = 8.5 - \log \frac{[NH_3]}{[NH_4^+]} \qquad \frac{[NH_3]}{[NH_4^+]} = 0.158$$

then,

$$\frac{[N_T]}{[NH_4^+]} = \frac{[NH_4^+]}{[NH_4^+]} + \frac{[NH_3]}{[NH_4^+]} \rightarrow \quad \frac{[N_T]}{[NH_4^+]} = 1 + 0.158$$

$[N_T] = 2000$ mg/L $= 1.158\,[NH_4^+]$ $\qquad [NH_4^+] = 1727$ mg/L

$[NH_3] = 273$ mg/L

Gas phase ammonia concentration, determined using Henry's Constant:

$$K_H^\circ = \frac{\text{moles } NH_3\text{-N} / L_{air}}{\text{moles } NH_3\text{-N} / L_{water}} = 7.2 \times 10^{-4} \qquad 14 \text{ g/mole (molecular wt. of N)}$$

$$\frac{273 \text{ mg } NH_3\text{-N} / L_{water}}{14 \text{ g/mole}} \cdot 7.2 \times 10^{-4} = \frac{X \text{ mg } NH_3\text{-N} / L_{air}}{14 \text{ g/mole}}$$

$X = 0.197$ mg NH_3-N / L_{air} = **0.197 g NH_3-N /m^3**

Empty bed contact time (EBCT):

$$EBCT = \frac{\text{reactor bed volume (L)}}{\text{air flow rate (L/min)}} = 0.5 \text{ min} = \mathbf{30\ s}$$

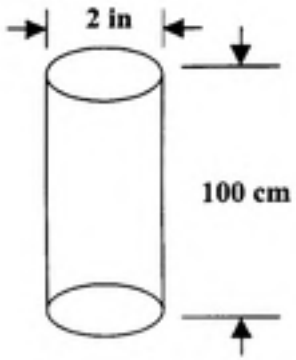
selected based on typical biofilter operating conditions

reactor volume: 2 in diameter
1 in (2.54 cm) radius

$\pi r^2 h = \pi(2.54 \text{ cm})^2 \cdot 100 \text{ cm}$

$= 2027 \text{ cm}^3 = 2.03 \text{ L}$

$$\text{air flow rate} = \frac{2.03 \text{ L}}{0.5 \text{ min}} = \mathbf{4.05\ L/min}$$



Volumetric loading rate:

$0.197 \text{ g } NH_3\text{-N}/m^3 = 1.97 \times 10^{-4} \text{ kg } NH_3\text{-N}/m^3 \rightarrow$ gas phase ammonia concentration

$$\frac{\text{gas phase ammonia concentration}}{\text{EBCT}} = \frac{1.97 \times 10^{-4} \text{ kg/m}^3}{0.5 \text{ min}} = 3.94 \times 10^{-4} \text{ kg/m}^3\text{min}$$

$$= \mathbf{0.567\ kg/m^3 \cdot d}$$

Sodium Hydroxide (NH_4OH) loading rate:

Air concentration of ammonia x Daily air flow = Required ammonia (NH_3-N)

$0.197 \text{ g } NH_3\text{-N}/m^3 \times 5.83 \text{ m}^3/\text{d} = \mathbf{1.15\ g\ NH_3\text{-N}/d}$

* Note this is the NH_3-N Mass Loading Rate

Assuming the complete conversion of NH_4OH to NH_3-N

$$1.15 \text{ g } NH_3\text{-N/d} \times \frac{17 \text{ g/mol } NH_3}{14 \text{ g/mol } NH_3\text{-N}} = 1.39 \text{ g } NH_3\text{/d}$$

NH_4OH solution is 30% NH_3 in water and has a density of 0.9 g/mL

1.39 g NH_3 /d / 0.30 = 4.65 g NH_4OH solution /d

4.65 g NH_4OH solution /d / 0.9 g/mL = **5.16 mL** of NH_4OH solution /d

Alkalinity Load:

1.15 g NH_3-N /d x (3.57 g alkalinity ($CaCO_3$) / g NH_3-N) = 4.07 g $CaCO_3$ /d

1 equivalent of alkalinity = 50 g $CaCO_3$; from 100 g/mol $CaCO_3$ x 2 eq/mol

then,

4.07 g $CaCO_3$ /d / 50 g $CaCO_3$ /eq = 0.0813 eq/d

Sodium bicarbonate ($NaHCO_3$) is used to provide the alkalinity

1 mole $NaHCO_3$ = 1 equivalent

= 84 g

0.0813 eq/d x 84 g $NaHCO_3$ /eq = 6.84 g $NaHCO_3$ /d

If the liquid flow is approximately 3.4 L/d, this provides a sodium bicarbonate concentration requirement of 2 g $NaHCO_3$ /L of supplemental water. However, since the liquid flow fluctuates slightly, the concentration is increased to **2.1 g $NaHCO_3$ /L**.

BIOLITE™ MEDIA AMMONIA ADSORPTION-DESORPTION.

Triplicate samples:	25 mL volume of media
sample 1	18.69 g
sample 2	18.80 g
sample 3	18.65 g

Samples are added to 15 mL of supplemental water solution
(aerated tap water with $NaHCO_3$ concentration of 2.16 g/L)

The daily ammonia feed is approximately 500 mg/d for Period 1; into 2 L of media.

Establishing a mass proportionality:

500 mg . . 2000 mL media
X . . 25 mL media

$X = 6.25$ mg NH_3-N

Samples are contained in 40 mL vials. A trial with deionized water determined that 25 mL of media required 35 mL of water to completely fill the samples vial, eliminating any headspace.

Thus,

$$6.25 \text{ mg } NH_3\text{-N} \,/\, 35 \text{ mL solution} = 0.178 \text{ mg } NH_3\text{-N /mL}$$
$$= 0.178 \text{ g } NH_3\text{-N /L}$$

$$0.178 \text{ g } NH_3\text{-N /L} \times \frac{14 \text{ g } NH_3\text{-N /mol}}{53.5 \text{ g } NH_4Cl \text{ /mol}} = 0.682 \text{ g } NH_4Cl \text{ /L}$$

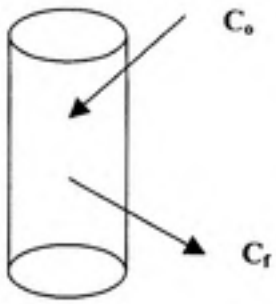
0.341 g NH_4Cl and 1.08 g $NaHCO_3$ were added to 500 mL of dechlorinated tap water to make the sample solution. Three control vials (no media) were filled to eliminate headspace, stored, and analyzed along with the sample vials.

q = ammonia in the media (mg NH_3-N /mg media)

w = weight of the media

C = ammonia in the solution (ng NH_3-N /L)

V = volume of water



Basic equation (conservation): $q_o w + C_o V = q_f w + C_e V$

Since q_f reaches equilibrium with C_e

$$q_f = kC_e, \qquad k = q_f / C_e$$

$$= \frac{\text{mg } NH_3\text{-N /mg media}}{\text{mg } NH_3\text{-N /L}}$$

$$= \text{L solution / mg media}$$

Deionized water control:

$q_o w + C_o V = q_f w + C_e V$ from basic equation; $C_o = 0$, let $q_f = kC_e$

$q_o w = kC_e w + C_e V$

$q_o w = C_e (V + kw)$

$$q_o = \frac{C_e (V + kw)}{w}$$

Triplicate samples: (note- s subscript distinguishes sample parameters)

$q_o w_s + C_{os} V_s = q_f w_s + C_{es} V_s$ from basic equation; let $q_f = kC_e$; substitute in q_o from above

$$\frac{C_e (V + kw)}{w} \times w_s + C_{os} V_s = C_{es} (kw_s + V_s)$$

Since the volume of water and mass of media were not measured for the deionized water control, they are assumed the same as the averaged triplicate sample parameters. This is acceptable due to the low standard deviation in the sample parameters.

$w = w_s$
$V = V_s$

$$\frac{C_e (V + kw)}{w} \times w + C_{os} V = C_{es} (kw + V)$$

$C_e (V + kw) + C_{os} V = C_{es} (V + kw)$

$kC_e w + C_e V \; C_{os} V = C_{es} V + kC_{es} w$

$kC_e w - kC_{es} w = C_{es} V - C_e V - C_{os} V$

$$k = \frac{V(C_{es} - C_e - C_{os})}{w (C_e - C_{es})}$$

Substituting in the following measured quantities

$V = 0.035$ L
$w = 18.7$ g media

$C_{es} = 200.6$ mg NH_3-N /L
$C_e = 29.6$ mg NH_3-N /L
$C_{os} = 178.6$ mg NH_3-N /L
0.035 L x (200.6 - 29.6 - 178.6) mg NH_3-N /L

$$k = \frac{18.7\ g \times (29.6 - 200.6)\ mg\ NH_3\text{-}N\ /L}{0.035\ L \times (-7.6)\ mg\ NH_3\text{-}N\ /L \over 18.7\ g \times (-171)\ mg\ NH_3\text{-}N\ /L}$$

$$\mathbf{k} = \frac{0.266\ L}{3197.7\ g} = 8.3 \times 10^{-5}\ L/g\ media = \mathbf{0.083\ mL/g\ media}$$

Substituting k back into the equation for q_o:

$$\mathbf{q_o = 0.058\ mg\ NH_3\text{-}N\ /\ g\ media}$$

Using the density of the media obtained from the triplicate samples:

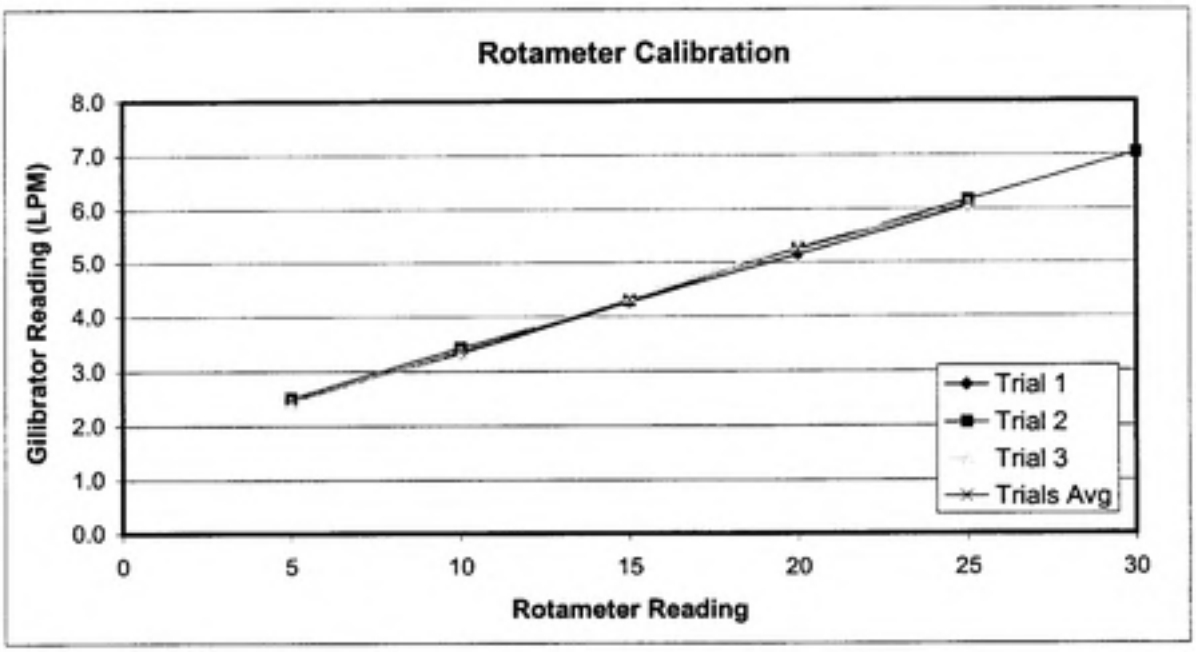
$$\frac{25\ mL\ media\ volume}{18.7\ g\ media} \times 2027\ mL = 1516\ g\ media\ (in\ the\ columns)$$

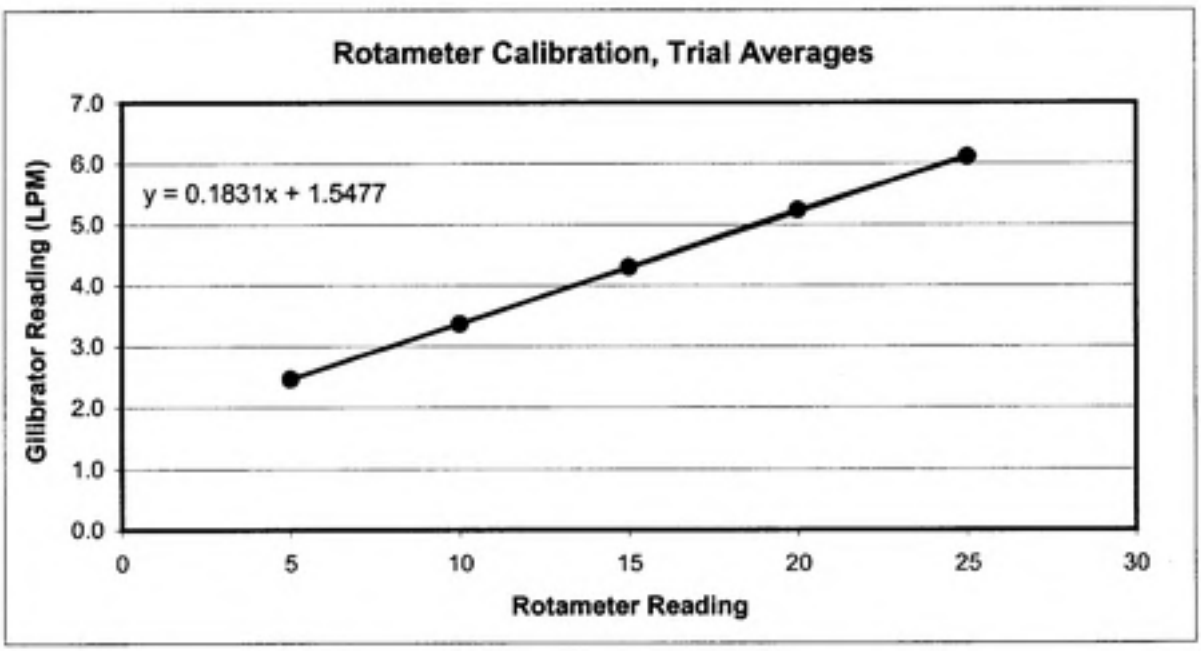
Then, the initial ammonia content in the biotrickling filter media:

$$0.058\ mg\ NH_3\text{-}N/g\ media \times 1516\ g\ media = \mathbf{87.7\ mg\ NH_3\text{-}N}$$

APPENDIX B

Rotameter Calibration (Cole Palmer SN: 139354)
6 September 1999





Rotameter Calibration (Cole Palmer SN: 139354)
6 September 1999

Gilibrator Primary Flow Calibrator, PN: 800268, SN: 6778-B
Bubble Generator (High), PN: 800285, SN: 9903-H
Range 2-30 LPM
Calibration: 20 March 1991

Rotameter Reading	Gilibrator Reading (LPM)										
	Average	Reading 1 through 10									
Trial 1 (pulse dampener @ 3 psi)											
5	2.445	2.443	2.448	2.443	2.446	2.444	2.446	2.445	2.447	2.444	2.446
10	3.327	3.330	3.326	3.326	3.327	3.327	3.326	3.326	3.327	3.327	3.328
15	4.264	4.265	4.260	4.263	4.265	4.263	4.265	4.263	4.263	4.266	4.262
20	5.144	5.150	5.144	5.144	5.144	5.142	5.142	5.144	5.143	5.145	5.144
25	6.060	6.068	6.061	6.059	6.056	6.063	6.058	6.059	6.063	6.058	6.058
Trial 2 (pulse dampener @ 5 psi)											
5	2.509	2.513	2.513	2.511	2.510	2.510	2.507	2.507	2.508	2.507	2.506
10	3.426	3.422	3.424	3.428	3.426	3.426	3.429	3.424	3.427	3.426	3.429
15	4.286	4.285	4.281	4.286	4.284	4.288	4.285	4.290	4.285	4.289	4.286
20	5.261	5.258	5.257	5.257	5.265	5.261	5.261	5.262	5.261	5.263	5.262
25	6.165	6.166	6.173	6.159	6.158	6.166	6.166	6.165	6.163	6.165	6.168
30	7.036	7.037	7.037	7.037	7.032	7.041	7.032	7.037	7.035	7.044	7.026
Trial 3 (pulse dampener @ 3 psi)											
5	2.427	2.424	2.427	2.428	2.427	2.424	2.429	2.429	2.427	2.428	2.429
10	3.348	3.345	3.347	3.346	3.350	3.349	3.347	3.349	3.348	3.349	3.350
15	4.362	4.365	4.363	4.362	4.359	4.362	4.362	4.360	4.362	4.367	4.360
20	5.310	5.318	5.312	5.310	5.301	5.315	5.313	5.314	5.305	5.313	5.303
25	6.083	6.081	6.100	6.086	6.070	6.090	6.081	6.083	6.081	6.079	6.083

Trial Average

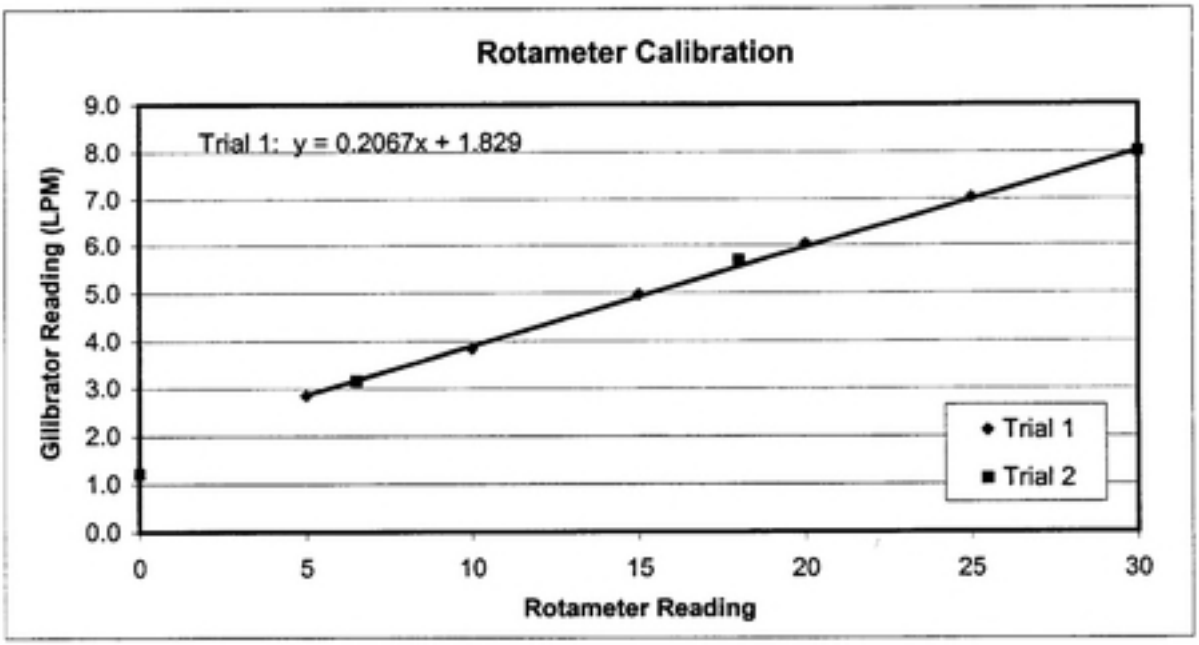
5	2.461	2.445	2.509	2.427
10	3.367	3.327	3.426	3.348
15	4.304	4.264	4.286	4.362
20	5.238	5.144	5.261	5.310
25	6.103	6.060	6.165	6.083

Airflow Calibration (Cole Parmer SN: 139354)
13 November 1999

Gilibrator Primary Flow Calibrator, PN: 800268, SN: 6778-B
Bubble Generator (High), PN: 800285, SN: 9903-H
Range 2-30 LPM
Calibration: 20 March 1991

Rotameter Reading	Gilibrator Reading (LPM)										
	Average	Reading 1 through 10									
Trial 1 (pulse dampener @ 5 psi, rotameter set to 37)											
Effluent Column 2	8.617	8.610	8.627	8.603	8.623	8.633	8.606	8.616	8.627	8.616	8.606
Between Columns	8.649	8.627	8.647	8.671	8.647	8.667	8.647	8.633	8.643	8.667	8.640
Influent Column 1	8.666	8.667	8.657	8.681	8.678	8.654	8.671	8.660	8.667	8.660	8.667
Rotameter Effluent	7.883	7.894	7.886	7.888	7.880	7.874	7.880	7.877	7.886	7.891	7.877
Trial 2 (pulse dampener @ 4 psi, rotameter set to 13)											
Effluent Column 2	4.534	4.536	4.543	4.532	4.534	4.532	4.533	4.532	4.532	4.534	4.532
Between Columns	4.550	4.553	4.511	4.541	4.545	4.554	4.557	4.556	4.559	4.562	4.558
Influent Column 1	4.574	4.575	4.578	4.578	4.575	4.574	4.577	4.575	4.578	4.566	4.567

Rotameter Calibration (Cole Parmer SN: 139354)
23 November 1999



Rotameter Calibration (Cole Parmer SN: 139354)
23 November 1999

Gilibrator Primary Flow Calibrator, PN: 800268, SN: 6778-B
Bubble Generator (High), PN: 800285, SN: 9903-H
Range 2-30 LPM
Calibration: 20 March 1991

Rotameter Reading	Pressure (psi)	Gilibrator Reading (LPM)										
		Average	Reading 1 through 10									
Trial 1												
5	15.0	2.842	2.842	2.844	2.843	2.843	2.844	2.843	2.843	2.840	2.839	2.841
10	14.0	3.836	3.838	3.834	3.833	3.834	3.834	3.840	3.841	3.843	3.827	3.832
15	12.0	4.972	4.970	4.966	4.969	4.971	4.963	4.979	4.977	4.973	4.977	4.972
20	9.8	6.032	6.031	6.035	6.039	6.026	6.028	6.025	6.028	6.026	6.045	6.036
25	7.5	7.035	7.028	7.046	7.032	7.028	7.037	7.026	7.037	7.037	7.036	7.038
30	5.0	8.047	8.050	8.049	8.053	8.035	8.062	8.053	8.044	8.038	8.047	8.038
32	4.9	8.354	8.353	8.349	8.355	8.365	8.371	8.352	8.339	8.365	8.339	8.352

Pulse dampener initially set at 4.9 psi, pressure release value set at 15 psi.

Trial 2												
32	4.9	8.354	8.353	8.349	8.355	8.365	8.371	8.352	8.339	8.365	8.339	8.352
30	4.5	8.011	7.999	8.026	8.026	8.006	8.015	8.020	8.003	8.003	8.015	8.000
18	4.0	5.681	5.663	5.674	5.665	5.686	5.687	5.687	5.684	5.689	5.684	5.689
6.5	3.5	3.154	3.157	3.156	3.159	3.170	3.150	3.151	3.151	3.146	3.149	3.150
0.0	3.0	1.216	1.210	1.213	1.213	1.214	1.217	1.217	1.216	1.218	1.219	1.219

Rotameter set to maximum (completely open), pulse dampener pressure adjusted.

APPENDIX C

Operator Log, Week of _____

ITEM	MON.	TUE.	WED.	THU.	FRI.	SAT.	SUN.
Operator initials							
Time of day							
Humidification flask: water level (ok/lo)							
Ammonia flask: water level (ok/lo)							
Syringe volume (mL)							
NH4OH added (mL)							
Source pressure (psig)							
Adjusted pressure?							
Rotameter reading							
Adjusted reading?							
Headloss column 1 (cm)							
Headloss column 2 (cm)							
Ambient temperature (C)							
Amb. rel. humidity (%)							
Column 2 exhaust temp. (C)							
Col. 2 exh. rel. humidity (%)							
Water level influent (L)							
Water level intermediate (L)							
Water level effluent (L)							
pH column 1 influent							
pH column 1 effluent							
pH column 2 influent							
pH column 2 effluent							
Notes							

Study Sampling Schedule

Month	Sun	Mon	Tue	Wed	Thr	Fri	Sat
Oct						15	16
Oct	17 SC-1	18	19	20 SC-1	21	22 SC-1	23 SS
Oct	24	25 SC	26 SC	27 SC	28	29 SC-1	30
Oct/Nov	31	1 SC-1	2	3 SC	4	5 SC-1	6 SS
Nov	7	8 SC	9 SC	10 SC		12 SC-1	13
Nov	14	15 SC-1	16	17 SC	18	19 SC-1	20 SS
Nov	21	22 SC					

Legend:

SC = Standard Collection = air (NH_3) & water (NH_3, NO_x, NO_2)

SC-1 = Standard Collection without NO_2 = air (NH_3) & water (NH_3, NO_x)

SS = Suspended Solids

APPENDIX D

Ammonia Nitrogen Analyses in Air and Water: Nessler Method

12 November 1999

Table 1. Calibration Data

Standard NH3 (mg/L)	Absorbance
0.0	0.040
1.0	0.266
2.0	0.493

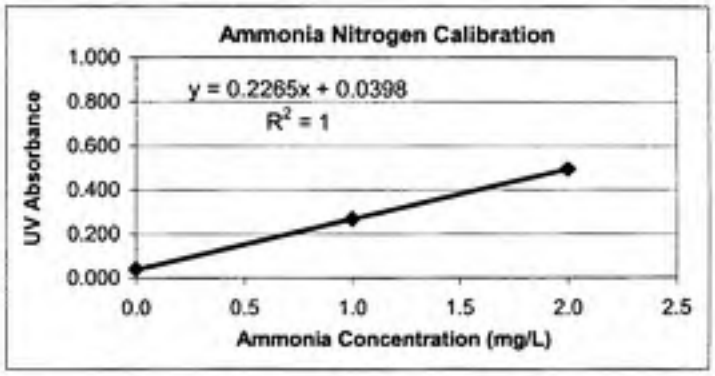


Table 2. Ammonia Concentrations in the Water Sample

Sample	Column 1 Effluent		Column 2 Influent		Column 2 Effluent	
Dilution	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)
1:1	RD		0.530	2.2	0.049	0.04
			0.539	2.2	0.048	0.04
1:5	0.456	9.2	0.129	2.0	<MDL	
	0.461	9.3				
1:10	0.250	9.3	<MDL			
	0.250	9.3				

RD = required dilution <MDL = less than the method detection limit

Apparatus zeroed at the end of the analysis to ± 0.002.

Column 1 Influent absorbance 0.042 = 0.01 mg/L of ammonia in the source water.

Table 3. Ammonia in Boric Acid Solution

Sample	Column 1 Influent	
Dilution	Abs	NH3 (mg/L)
1:5	RD	
1:10	RD	
1:50	0.227	41.3

Sample	Column 2 Influent		Column 2 Effluent*	
Dilution	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)
1:1	0.073	0.1	0.092	0.2
1:5	<MDL		<MDL	

RD = required dilution <MDL = less than method detection limit

*Samples produced an orange precipitate. Measurements acquired after precipitate settled.

Table 4. Ammonia in Air

Sample	Sample NH3 (mg/L)	Sample Time (min)	Air NH3 (mg/L)
C1 Influent	41.3	6.25	0.073
C2 Influent	0.1	90.00	1.8E-05
C2 Effluent	0.2	120.00	2.1E-05

Rotameter = 35

Air flow = 9.1 L/min

Nitrite Analyses in Water: Ferrous Sulfate Method

10 November 1999

Table 1. Calibration Curve

Standard NO2 (mg/L)	Absorbance
0.0	0.000
74.1	0.189
148.1	0.390

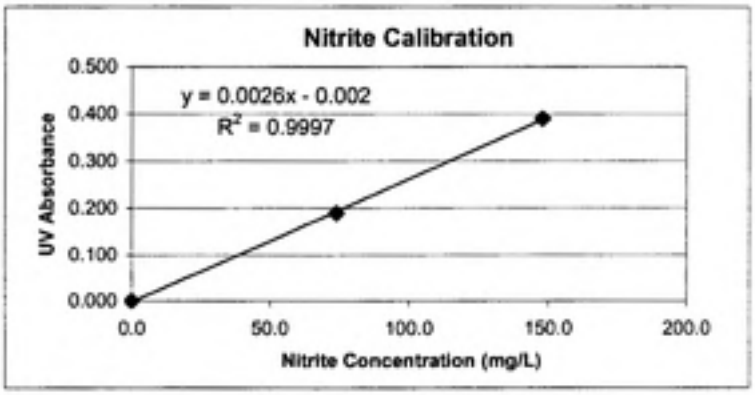


Table 2. Nitrite Concentrations in the Water Sample

Sample	Column 1 Effluent		Column 2 Influent		Column 2 Effluent	
Dilution	Abs	NO_2^--N (mg/L)	Abs	NO_2^--N (mg/L)	Abs	NO_2^--N (mg/L)
1:1	RD		RD		0.005	2.7
1:2	0.275	213.1	0.311	240.8		

RD = required dilution <MDL = less than the method detection limit

Apparatus zeroed at the end of the analysis to ± 0.002.

Stock Solution:

$NaNO_2$ diluted in 100mL of deionized water: 0.1111 g

Stock Concentration: 741 mg/L

Oxidized Nitrogen Analyses in Water: Nitrate Cadmium Reduction Method

16 November 1999

Table 1. Calibration Curve

Standard NOx (mg/L)	Absorbance
0.0	0.054
8.0	0.132
16.0	0.181
24.0	0.235

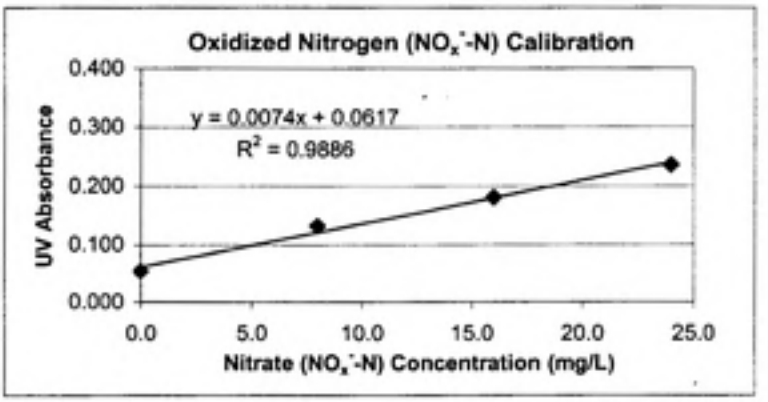


Table 2. Nitrite Concentrations in the Water Sample

Sample	Column 1 Effluent		Column 2 Influent		Column 2 Effluent	
Dilution	Abs	NO_x^--N (mg/L)	Abs	NO_x^--N (mg/L)	Abs	NO_x^--N (mg/L)
1:16.7			0.175	255.7		
1:25	0.162	338.9			0.168	359.1

RD = required dilution <MDL = less than the method detection limit

Apparatus zeroed at the end of the analysis to ± 0.005.

Media Adsorption-Desorption of Ammonia Nitrogen Analyses: Nessler Method
3 December 1999

Table 1. Calibration Curve

Standard NH3 (mg/L)	Absorbance
0.0	0.039
1.0	0.267
2.0	0.503

22 Nov 1999 Calibration

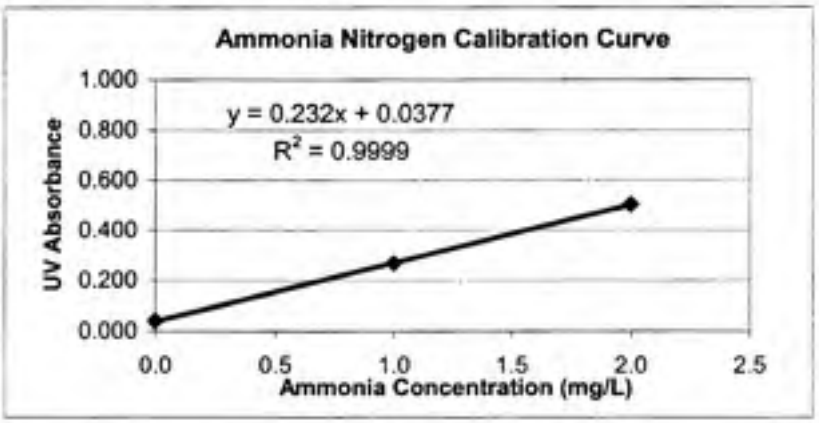


Table 2. Ammonia Concentrations in the Samples with Ammonia Solution

Sample	Sample 1		Sample 2		Sample 3	
Dilution	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)
1:100	0.504	201	0.503	201	0.502	200

25 mL of new media used in each sample

Table 3. Ammonia Concentrations in the Controls with Ammonia Solution

Sample	Control 1		Control 2		Control 3	
Dilution	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)	Abs	NH3 (mg/L)
1:100	0.467	185	0.463	183	0.457	181

Table 4. Ammonia Concentration in the Sample Media and DI Water

Sample	DI Water	
Dilution	Abs	NH3 (mg/L)
1:1	RD	
1:50	0.175	29.59

25 mL of new media used in the sample
RD = required dilution

	Samples			Controls	
	NH3 (mg/L)	Media (mg)	Solution (mL)	NH3 (mg/L)	Solution (mL)
Mean	200.6	18.71	35.83	183.0	48.03
Std Dev	0.4	0.07	0.21	2.2	0.29

1. 25 mL of new media in a 178.6 mg/L solution increased the NH_3-N concentration by 17.0 mg/L
2. There was a 5 mg/L discrepancy between the original solution and analyzed controls
3. 25 mL of new media in DI water increased the NH_3-N concentration by 29.6 mg/L

APPENDIX E

Table E1. Experimental Data

	Date	Time				Ambient		Vessels						Ammonia (NH_4OH)							
								Influent		Intermediate		Effluent		Syringe		Calculated Feed				Measured Feed	
		Log	Elapsed	Elapsed	Format	Temp	Humid	Level	Δ	Level	Δ	Level	Δ	Added	Reading	Dose	NH_3-N			NH_3-N	
				min	min	°C	%	L	L	ml	ml	L	L	ml	ml	ml	mg	mg/d	mg/L	mg/L	mg/d
Seed	11 Oct	08:30				22.5	64	14.0							15.0						
	12 Oct	14:10	29:40	1780	1780	24.1	54	14.5							13.0	2.0	445	360	0.061	0.045	293
	13 Oct	14:10	24:00	1440	1440	21.6	56	14.5							10.0	3.0	667	667	0.103		
	14 Oct	09:00	18:50	1130	1130	23.6	40	14.5	6.5						8.0	2.0	445	567	0.087	0.044	286
Period 1	15 Oct	08:30	23:30	1410	1410	23.9	37	15.0							5.0	3.0	667	681	0.110		
	16 Oct	12:15	27:45	1665	1665	22.7	65	7.0	14.0					18.0	2.0	3.0	667	577	0.083		
	17 Oct	12:55	24:40	1480	1480	24.4	78	14.0							18.0	2.0	445	433	0.073	0.049	319
	18 Oct	17:05	28:10	1690	1690	23.7	41		15.0						15.0	3.0	667	568	0.087		
	19 Oct	18:10	25:05	1505	1505	22.9	52	14.0							12.5	2.5	556	532	0.084		
	20 Oct	11:00	16:50	1010	1010	22.0	56	11.3							11.0	1.5	334	476	0.075	0.040	260
	21 Oct	15:00	28:00	1680	1680	21.6	39	7.0						-1.5	8.5	2.5	556	476	0.073		
	22 Oct	17:00	26:00	1560	1560	22.8	43	3.5	16.5						5.5	1.5	334	308	0.050	0.033	215
	23 Oct	09:20	16:20	980	980	23.3	32	18.0						16.0	4.0	1.5	334	490	0.066		
	24 Oct	09:45	24:25	1465	1465	23.2	30	14.5							18.0	2.0	445	437	0.072		
	25 Oct	08:00	22:15	1335	1335	21.3	30	11.2							16.0	2.0	445	480	0.072	0.030	195
Period 2	25 Oct	18:30	10:30	630	630			9.5							15.0	1.0	222	508	0.078		
	26 Oct	09:45	15:15	915	945	23.6	32	6.9							12.0	3.0	667	1016	0.153	0.039	254
	27 Oct	13:00	27:15	1635	1635	23.8	34	3.0	18.3						6.5	5.5	1223	1077	0.170	0.207	1346
	28 Oct	15:00	26:00	1560	1560	22.4	34	18.0						19.0	1.0	5.5	1223	1129	0.174		
	29 Oct	13:15	22:15	1335	1335	24.9	40	15.0							17.0	3.0	667	720	0.101	0.001	7
	30 Oct	11:30	22:15	1335	1335	25.1	40	11.8		900		8.0			13.7	3.3	734	791	0.125		
	31 Oct	10:40	23:10	1390	1390	24.1	67	8.8		870		9.0			8.8	4.9	1090	1129	0.174		
	1 Nov	11:45	25:05	1505	1505	22.8	51	5.5				12.0		16.0	4.0	4.8	1067	1021	0.157	0.070	455
	2 Nov	12:30	24:45	1485	1485	24.0	66	2.5	18.0			15.0	-9.0		16.0	4.0	889	862	0.136		
	3 Nov	11:40	23:10	1390	1390	23.7	25	17.8				8.5			11.5	4.5	1001	1037	0.156	0.137	891
	4 Nov	09:05	21:25	1285	1285	26.7	25	15.8		2450	-200	10.5			7.0	4.5	1001	1121	0.181		
	5 Nov	16:00	30:55	1855	1855	23.4	28	11.7		2050	-200	14.0		19.0	1.0	6.0	1334	1036	0.159	0.095	618
	6 Nov	15:45	23:45	1425	1425	25.2	41	8.5		1650	-50	17.5	-13.5		16.5	3.5	778	786	0.127		
	7 Nov	15:36	23:51	1431	1431	24.4	30	5.7		1500	-50	8.2			12.0	4.5	1001	1007	0.220		
	8 Nov	12:40	21:04	1264	1264	22.8	29	3.3	14.0	1250	-50	10.0			8.0	4.0	889	1013	0.156	0.080	520
Period 3	8 Nov	18:00	5:20	320	320			16.7			-50				7.0	1.0	222	1001	0.096		
	9 Nov	10:05	16:05	965	965	23.8	46	14.8		900	900	12.7		16.0	4.0	3.0	667	995	0.090	0.044	456
	10 Nov	13:00	26:55	1615	1615	22.7	46	10.8		1550	-100	16.0	-10.0		15.0	5.0	1112	991	0.088	0.028	290
	11 Nov	16:30	27:30	1650	1650	23.1	59	7.0		1300	-50	9.0			10.0	5.0	1112	970	0.081		
	12 Nov	16:30	24:00	1440	1440	21.7	45	3.6	17.3	1200	900	12.4			5.3	4.7	1045	1045	0.080	0.073	953
	13 Nov	11:40	19:10	1150	1150	23.2	48	19.0		2100	-50	14.5	-8.5	18.5	1.5	3.8	845	1058	0.079		
	14 Nov	14:10	26:30	1590	1590	25.6	40	14.9		2050	-50	10.0			15.0	5.0	1112	1007	0.079		
	15 Nov	14:00	23:50	1430	1430	22.3	27	11.2		2050	-150	13.0		-0.6	14.5	0.5	111	112	0.009	--	
	16 Nov	13:04	23:04	1384	1384	23.0	23	7.8		1900	-100	16.0			9.5	4.4	978	1018	0.081	0.030	383
	17 Nov	12:40	23:36	1416	1416	22.8	22	4.4	16.6	0	1900	16.3	-12.3	15.2	4.8	4.7	1045	1063	0.084	0.030	383
	18 Nov																				
	19 Nov	08:35	43:55	2635	2635	23.0	26	14.8		1700	-50	11.8			12.8	7.2	1601	875	0.072	0.026	316
	20 Nov	13:45	29:10	1750	1750	23.5	52	10.5		1600	-50	15.5	-9.5	13.0	7.0	5.8	1290	1061	0.081		
	21 Nov	13:45	26:00	1560	1560	23.8	56	7.0		1600	-125	9.3			14.8	5.2	1156	1067	0.091		
	22 Nov	10:50	19:05	1145	1145	23.1	73	4.7		1100		11.3			11.0	3.8	845	1063	0.090	0.057	676

Table E1.

	Date	Air								Headloss		Effluent		Water										
		Pump	Rotameter			Flow								Pump		Column 1					Column 2			
		Press	Setting	Reading	Avg	Setting	Reading	Avg	(elapsed)	Col 1	Col 2	Temp	Humid	Setting	$[NaHCO_3]$	Elapsed	Flow	pH		SS	Elapsed	Flow	pH	
		psi	#	#	#	L/min	L/min	L/min	L	cm H2O	cm H2O	°C	%	L/d	g/L	L	L/d	In	Out	mg/L	L	L/d	In	Out
Seed	11 Oct	5.0	13	10	11.5	4.5	3.9	4.2	0	2.0	1.5	23.8	93	7.0				7.69	6.96				7.69	7.94
	12 Oct	4.0	13	9	11.0	4.5	3.7	4.1	7303	2.1	1.9	23.6	93	7.0				6.67	6.67				6.67	6.35
	13 Oct	5.0	13	13	13.0	4.5	4.5	4.5	6503	2.1	2.0	21.2	93	7.0				7.14	6.68				7.14	6.23
	14 Oct	4.5	13	13	13.0	4.5	4.5	4.5	5103	2.0	2.0	23.5	91	7.0				6.66	6.43				6.43	5.90
Period 1	15 Oct	4.5	13	11	12.0	4.5	4.1	4.3	6076	2.5	1.5	23.6	87	7.0	0.54	6.0	6.1		8.01				7.84	8.25
	16 Oct	4.5	13	16	14.5	4.5	5.1	4.8	8035	2.1	2.0	24.4	91	7.0	0.54	8.0	6.9	8.30	8.37				7.85	8.02
	17 Oct	5.0	13	9	11.0	4.5	3.7	4.1	6072	2.2	2.0	23.6	93	7.0	0.54	7.0	6.6	8.60	8.16				7.71	8.10
	18 Oct	4.2	13	13	13.0	4.5	4.5	4.5	7632	2.1	0.7	23.1	92	7.0	0.54				7.95				7.41	7.95
	19 Oct	4.0	13	12	12.5	4.5	4.3	4.4	6641	2.1	2.0	22.7	89	3.6	1.08	15.0	6.8		8.16				7.63	8.41
	20 Oct	4.0	13	12	12.5	4.5	4.3	4.4	4457	2.5	2.0	21.3	93	3.8	1.08	2.7	3.8	8.27	7.78				7.74	8.27
	21 Oct	4.0	13	13	13.0	4.5	4.5	4.5	7587	2.1	1.7	21.1	93	3.6	1.08	4.3	3.7	8.34	8.09				7.83	8.46
	22 Oct	4.0	13	11	12.0	4.5	4.1	4.3	6723	2.1	1.4	21.8	50	3.6	1.08	3.5	3.2	8.41	8.32					8.42
	23 Oct	4.0	13	19	16.0	4.5	5.8	5.1	5033	1.9	1.8	22.8	92	3.6	1.08	2.0	2.9	8.47	8.22			0.9	8.00	8.42
	24 Oct	4.0	13	10	11.5	4.5	3.9	4.2	6162	2.0	1.9	22.7	91	3.6	1.08	3.5	3.4		8.10				8.10	8.26
	25 Oct	4.0	13	14	13.5	4.5	4.7	4.6	6167	2.6	1.7	21.3	92	3.6	1.08	3.3	3.6	8.49	8.12					8.24
Period 2	25 Oct		13	13	13.0	4.5	4.5	4.5	2845					3.6	2.16	1.7	3.9							
	26 Oct	4.0	13	14	13.5	4.5	4.7	4.6	4365	2.1	2.0	23.6	89	3.6	2.16	2.6	4.0	8.29	8.35					8.74
	27 Oct	4.0	13	12	12.5	4.5	4.3	4.4	7215	2.3	1.8	22.8	45	3.6	2.16	3.9	3.4	8.06	8.04					8.48
	28 Oct	4.0	13	13	13.0	4.5	4.5	4.5	7045	1.3	1.2	21.4	91	3.6	2.16	3.3	3.0	8.61	7.64				8.67	8.80
	29 Oct	4.1	13	17	15.0	4.5	5.3	4.9	6581	2.0	1.6	24.6	78	3.6	2.16	3.0	3.2	8.58	8.57					8.37
	30 Oct	5.5	13	12	12.5	4.5	4.3	4.4	5891	2.0	1.6	23.6	93	3.6	2.16	3.2	3.5	8.63	8.26				8.48	8.78
	31 Oct	7.0	13	13	13.0	4.5	4.5	4.5	6277	3.4	1.9	24.3	92	3.6	2.16	3.1	3.2	8.71	8.35	3.0	3.1		8.34	8.70
	1 Nov	4.0	13	13	13.0	4.5	4.5	4.5	6797	2.2	1.9	21.6	93	3.6	2.16	3.3	3.1	8.67	8.03	3.0	2.9		8.43	8.94
	2 Nov	4.0	13	12	12.5	4.5	4.3	4.4	6553	2.4	1.9	23.5	93	3.6	2.16	3.0	2.9	8.55	8.05	3.0	2.9		8.49	8.80
	3 Nov	3.7	13	14	13.5	4.5	4.7	4.6	6421	2.2	1.8	23.5	84	3.6	2.16	2.7	2.8	8.60	8.35	2.5	2.6		8.54	8.72
	4 Nov	3.9	13	11	12.0	4.5	4.1	4.3	5538	2.3	1.8	21.6	89	3.6	2.16	2.0	2.2	8.59	8.47	2.0	2.2		8.60	8.80
	5 Nov	4.0	13	13	13.0	4.5	4.5	4.5	8377	2.4	1.8	22.9	92	3.5	2.16	4.1	3.2	8.61	7.19	3.5	2.7		8.55	8.46
	6 Nov	3.8	13	11	12.0	4.5	4.1	4.3	6141	2.4	2.0	25.6	91	3.5	2.16	3.2	3.2	8.61	8.73	3.5	3.5	0.9	8.59	8.90
	7 Nov	2.8	13	0	6.5	4.5	1.8	3.2	4540	0.0	0.0	24.9	83	3.5	2.16	2.8	2.8	9.00	8.70	4.2	4.2		8.68	8.75
	8 Nov	4.0	13	13	13.0	4.5	4.5	4.5	5708	2.1	2.0	23.0	82	3.5	2.16	2.4	2.7	9.02	8.51	1.8	2.1		8.61	8.69
Period 3	8 Nov		26	26	26.0	7.2	7.2	7.2	2305					3.5	2.16	0.6	2.7							
	9 Nov	4.5	26	31	28.5	7.2	8.2	7.7	7450	3.2	2.5	23.2	88	3.5	2.16	1.9	2.6	8.70	7.71	2.7	3.0		8.58	8.31
	10 Nov	4.5	26	32	29.0	7.2	8.4	7.8	12635	3.4	2.6	23.2	91	3.5	2.16	4.0	3.6	8.73	8.30	3.3	2.9		8.34	8.74
	11 Nov	4.5	35	28	31.5	9.1	7.6	8.3	13761	4.2	3.0	23.2	89	3.5	2.16	3.8	3.3	8.68	8.15	3.0	2.6		8.21	8.73
	12 Nov	5.0	35	35	35.0	9.1	9.1	9.1	13051	4.4	3.2	21.2	93	3.5	2.16	3.4	3.4	8.90	7.95	3.4	3.4		8.02	8.25
	13 Nov	5.0	35	37	36.0	9.1	9.5	9.3	10661	4.3	3.3	23.4	89	3.2	2.16	1.9	2.4	8.57	8.31	2.1	2.6		8.15	8.83
	14 Nov	5.0	35	33	34.0	9.1	8.7	8.9	14062	4.5	3.3	25.4	93	3.5	2.16	4.1	3.7	8.64	8.46	4.0	3.6		8.35	8.84
	15 Nov	4.7	35	34	34.5	9.1	8.9	9.0	12813	4.3	3.3	22.7	92	3.5	2.16	3.7	3.7	8.61	9.24	3.0	3.0		8.70	9.22
	16 Nov	4.8	34	33	33.5	8.9	8.7	8.8	12115	4.8	3.4	22.0	87	3.5	2.16	3.4	3.5	8.78	8.70	3.0	3.1		8.43	8.83
	17 Nov	5.0	34	33	33.5	8.9	8.7	8.8	12395	4.8	3.4	21.8	94	3.5	2.16	3.4	3.5	9.00	8.63	2.3	2.3		8.52	8.87
	18 Nov																							
	19 Nov	4.7	32	32	32.0	8.4	8.4	8.4	22248	4.5	3.3	21.6	93	3.5	2.16	6.2	3.4	8.69	8.54	5.8	3.2		8.78	9.10
	20 Nov	5.0	35	35	35.0	9.1	9.1	9.1	15861	4.7	3.3	23.6	92	3.5	2.16	4.3	3.5	8.83	8.98	3.7	3.0	1.1	8.74	9.10
	21 Nov	4.9	31	30	30.5	8.2	8.0	8.1	12688	4.9	3.3	24.1	93	3.5	2.16	3.5	3.2	8.89	8.13	3.3	3.0		8.42	8.81
	22 Nov	4.9	31	31	31.0	8.2	8.2	8.2	9431	4.8	3.3	22.9	93	3.5	2.16	2.3	2.9	8.98	8.43	2.0	2.5		8.17	8.76

Table E2. Column 1 Calculations

Date	Time	Influent								Effluent								
		Air				Water		pH		Air		Water						pH
	(elapsed) min	C: NH3-N g	C: NH3-N mg/d	M: NH3-N mg/L	M: NH3-N mg/d	NH3-N mg/L	NH3-N mg/d	Measure	Adjust	NH3-N mg/L	NH3-N mg/d	NH3-N mg/L	NH3-N mg/d	NO2-N mg/L	NO2-N mg/d	NOX-N mg/L	NOX-N mg/d	Measure
11 Oct	0	0	0	--				7.69										6.96
12 Oct	1780	445	360	0.045	293			6.87	7.02									6.67
13 Oct	1440	667	667			0.5		7.14				22.4						6.68
14 Oct	1130	445	567	0.044	286			6.86		2.0E-03	13.01					124		6.43
15 Oct	1410	667	681															8.01
16 Oct	1665	667	577					8.70										8.37
17 Oct	1480	445	433	0.049	319	0.02	1.4E-01	8.60	8.30	1.5E-04	0.98	4.6	31.3			63.2	430.4	8.18
18 Oct	1690	667	568															7.95
19 Oct	1505	556	532															8.18
20 Oct	1010	334	476	0.040	260			8.27		1.2E-04	0.78	20.7	79.7			125.6	483.5	7.78
21 Oct	1680	556	476					8.34										8.09
22 Oct	1560	334	308	0.033	215	0.01	3.2E-02		8.41	1.6E-04	1.04	0.9	2.9			171.2	553.1	8.32
23 Oct	980	334	490					8.47										8.22
24 Oct	1465	445	437															8.10
25 Oct	1335	445	480	0.030	195	0.10	3.6E-01	8.49		1.6E-04	1.04	1.7	6.1	108	384.4	90.4	321.8	8.12
25 Oct	630	222	508															
26 Oct	945	667	1016	0.039	254			8.29		2.6E-04	1.82	7.0	27.7	180	713.1	220	871.6	8.35
27 Oct	1635	1223	1077	0.207	1346	0.01	3.4E-02	8.06	--	5.2E-04	3.38	14.0	48.1	179	614.8	124.8	428.7	8.04
28 Oct	1560	1223	1129					8.61										7.64
29 Oct	1335	667	720	0.001	7			8.58		1.5E-04	0.98	0.01	0.03			219.2	709.3	8.57
30 Oct	1335	734	791					8.63										8.26
31 Oct	1390	1090	1129					8.71										8.35
1 Nov	1505	1067	1021	0.070	455			8.87		1.5E-04	0.98	25.3	78.7			236.8	736.4	8.03
2 Nov	1485	889	862					8.91	8.55									8.05
3 Nov	1390	1001	1037	0.137	891	0.00	0.0E+00	8.60		2.5E-04	1.63	3.4	9.5	95	265.7	340	951.0	8.35
4 Nov	1285	1001	1121					8.59										8.47
5 Nov	1855	1334	1036	0.095	618			8.81		2.0E-04	1.30	44.9	142.9			465.6	1481.9	7.19
6 Nov	1425	778	786					8.81										8.73
7 Nov	1431	1001	1007					9.00										8.70
8 Nov	1264	889	1013	0.080	520	0.20	5.5E-01	9.02	8.61	2.1E-04	1.37	1.7	4.6	57	155.8	299.2	818.1	8.51
8 Nov	320	222	1001															
9 Nov	965	667	995	0.044	456	0.01	2.6E-02	8.70		6.0E-05	0.62	0.5	1.4	67	190.0	348	986.7	7.71
10 Nov	1615	1112	991	0.028	290			8.73		5.6E-05	0.58	1.5	5.3	64	226.3	255.2	910.2	8.30
11 Nov	1650	1112	970					8.88										8.15
12 Nov	1440	1045	1045	0.073	953	0.01	3.4E-02	8.90	8.50	2.1E-05	0.27	9.3	31.6		0.0	312.8	1063.5	7.95
13 Nov	1150	845	1058					8.57										8.31
14 Nov	1590	1112	1007					8.64										8.48
15 Nov	1430	111	112	--				8.61		--		0.1	0.4					9.24
16 Nov	1384	978	1018	0.030	383	0.10	3.5E-01	8.78		3.1E-05	0.40	0.09	0.3			272	962.2	8.70
17 Nov	1416	1045	1063	0.030	383	0.16	5.5E-01	9.00	8.48	8.6E-05	1.10	0.24	0.8	13	44.9	221.6	766.2	8.63
18 Nov																	0.0	
19 Nov	2635	1601	875	0.026	316			8.69		7.9E-05	0.96	0.13	0.4			211.2	715.6	8.54
20 Nov	1750	1290	1061					8.83										8.98
21 Nov	1560	1156	1067					8.89				6.24	20.2	187	604.2			8.13
22 Nov	1145	845	1063	0.057	676	0.12	3.5E-01	8.98		5.1E-05	0.60	0.91	2.6	241	697.1	360	1041.3	8.43

Table E3. Column 2 Calculations

Date	Time	Influent									Effluent								
		Air		Water							Air		Water						
	(elapsed) min	NH3-N mg/L	NH3-N mg/d	NH3-N mg/L	NH3-N mg/d	NO2-N mg/L	NO2-N mg/d	NOX-N mg/L	NOX-N mg/d	pH	NH3-N mg/L	NH3-N mg/d	NH3-N mg/L	NH3-N mg/d	NO2-N mg/L	NO2-N mg/d	NOX-N mg/L	NOX-N mg/d	pH
11 Oct	0																		7.94
12 Oct	1780																		6.35
13 Oct	1440			22.4									7.00						6.23
14 Oct	1130	2.00E-03	13.01							6.43							279.20		5.90
15 Oct	1410									7.84									8.25
16 Oct	1665									7.85									8.02
17 Oct	1480	1.5E-04	0.98	4.8	32.7			52	354.2	7.71	1.00E-04	0.65	0.01	0.07			125.60	855.44	8.10
18 Oct	1690									7.41									7.98
19 Oct	1505									7.63									8.41
20 Oct	1010	1.2E-04	0.78	--				98	378.8	7.74	1.10E-04	0.72	0.10	0.38			102.40	394.2	8.27
21 Oct	1680									7.83									8.45
22 Oct	1560	1.6E-04	1.04	0.3	1.0			111	359.3		7.30E-05	0.47	0.10	0.32			68.00	219.7	8.43
23 Oct	980									8.00									8.42
24 Oct	1465									8.10									8.26
25 Oct	1335	1.6E-04	1.04	--				--			1.20E-04	0.78	0.30	1.07	0.0	0.0	97.60	347.4	8.24
25 Oct	630																		
26 Oct	945	2.8E-04	1.82	4.4	17.4			227	900.1		8.00E-05	0.52	0.10	0.40	47.0	186.2	192.80	763.9	8.74
27 Oct	1635	5.2E-04	3.38	7.6	26.1						6.70E-05	0.44	0.10	0.34	3.0	10.3	64.00	219.8	8.48
28 Oct	1560									8.67									8.80
29 Oct	1335	1.5E-04	0.98	0.9	3.0			66	214.9	8.04	3.90E-04	2.54	0.88	2.85			208.00	673.1	8.37
30 Oct	1335									8.48									8.78
31 Oct	1390									8.34									8.70
1 Nov	1505	1.5E-04	0.98	1.1	3.2			306	877.2	8.43	1.20E-04	0.78	0.10	0.29			219.20	629.2	8.94
2 Nov	1485									8.49									8.80
3 Nov	1390	2.5E-04	1.63	1.0	2.6	0.0	0.0	256	663.0	8.54	2.60E-05	0.17	0.10	0.26	0.0	0.0	360.00	932.4	8.72
4 Nov	1285									8.60									8.80
5 Nov	1855	2.0E-04	1.30	1.3	3.5			46	123.9	8.55	1.10E-04	0.72	0.04	0.11			340.00	923.8	8.46
6 Nov	1425									8.59									8.90
7 Nov	1431									8.68									8.75
8 Nov	1264	2.1E-04	1.37	1.5	3.1			154	316.6	8.81	9.40E-05	0.61	0.10	0.21	1.0	2.1	204.80	420.0	8.89
8 Nov	320																		
9 Nov	965	6.0E-05	0.62	2.4	7.3	26.0	78.7	121	365.5	8.58	2.50E-05	0.26	0.10	0.30	1.0	3.0	267.20	808.5	8.31
10 Nov	1615	5.6E-05	0.58	3.9	11.5	72.0	211.9	211	621.4	8.34	2.30E-05	0.24	0.10	0.29	1.0	2.9	244.80	720.3	8.74
11 Nov	1650									8.21									8.73
12 Nov	1440	2.1E-05	0.27	2.2	7.5			236	802.4	8.02	2.10E-05	0.27	0.04	0.14			292.80	995.5	8.25
13 Nov	1150									8.15									8.83
14 Nov	1590									8.35									8.84
15 Nov	1430	--	0.00	1.7	5.1					8.70	--		0.10	0.30					9.22
16 Nov	1384	3.1E-05	0.40	1.06	3.3			190	594.3	8.43	3.50E-05	0.45	0.08	0.25			92.80	289.7	8.83
17 Nov	1416	6.6E-05	1.10	--	--	--	--	--	--	8.52	5.10E-05	0.65	0.10	0.23	1.0	2.3	299.20	699.8	8.87
18 Nov	0																		
19 Nov	2635	7.9E-05	0.96	0.15	0.5			231	732.8	8.78	3.10E-05	0.38	0.11	0.35			208.00	659.3	9.10
20 Nov	1750									8.74									9.10
21 Nov	1560			9.06	27.6					8.42			0.76	2.32	189.0	575.7			8.81
22 Nov	1145	5.1E-05	0.60	6.43	16.2	371.0	933.2	181	454.8	8.17	3.80E-05	0.45	0.23	0.58	226.0	568.5	326.40	821.0	8.76

Table E4. Column 1 Mass Calculations

	Date	Influent Air		Water	Effluent Air	Water			Total
		C:NH3-N mg/d	M:NH3-N mg/d	NH3-N mg/d	NH3-N mg/d	NH3-N mg/d	NO2-N mg/d	NOX-N mg/d	N mg/d
P1	17 Oct	433	319	0.14	0.98	31.3		430.4	462.7
	20 Oct	476	260		0.78	79.7		483.5	564.0
	22 Oct	308	215	0.03	1.04	2.9		553.1	557.1
	25 Oct	480	195	0.36	1.04	6.1	384.4	321.8	328.9
P2	26 Oct	1016	254	0.00	1.82	27.7	713.1	871.6	901.2
	27 Oct	1077	1346	0.03	3.38	48.1	614.8	426.7	666.3
	29 Oct	720	7		0.98	0.03		709.3	710.3
	1 Nov	1021	455		0.98	78.7		736.4	816.0
	3 Nov	1037	891	0.00	1.63	9.5	265.7	951.0	962.2
	5 Nov	1036	618		1.30	142.9		1481.9	1626.1
	8 Nov	1013	520	0.55	1.37	4.6	155.8	818.1	824.1
P3	9 Nov	995	456	0.03	0.62	1.4	190.0	986.7	988.7
	10 Nov	991	290		0.58	5.3	228.3	910.2	916.1
	12 Nov	1045	953	0.03	0.27	31.6		1063.5	1095.4
	16 Nov	1018	383	0.35	0.40	0.3		962.2	962.9
	17 Nov	1063	383	0.55	1.10	0.8	44.9	766.2	768.1
	19 Nov	875	316	0.00	0.96	0.4		715.6	717.0
	21 Nov	1067	0		0.00	20.2	604.2		20.2
	22 Nov	1063	676	0.35	0.60	2.6	697.1	1041.3	1044.6

Table E5. Column 2 Mass Calculations

	Date	Influent Air	Water			Total	Effluent Air	Water			Total
		NH3-N mg/d	NH3-N mg/d	NO2-N mg/d	NOX-N mg/d	N mg/d	NH3-N mg/d	NH3-N mg/d	NO2-N mg/d	NOX-N mg/d	N mg/d
P1	17 Oct	0.98	32.7		354.2	387.8	0.65	0.07		855.4	856
	20 Oct	0.78			378.8	379.6	0.72	0.38		394.2	395
	22 Oct	1.04	1.0		359.3	361.3	0.47	0.32		219.7	220
	25 Oct	1.04					0.78	1.07		347.4	349
P2	26 Oct	1.82	17.4		900.1	919.4	0.52	0.40	186.2	763.9	765
	27 Oct	3.38	26.1		0.0	29.5	0.44	0.34	10.3	219.8	221
	29 Oct	0.98	3.0		214.9	218.8	2.54	2.85		673.1	678
	1 Nov	0.98	3.2		877.2	881.3	0.78	0.29		629.2	630
	3 Nov	1.63	2.6	0.0	663.0	667.2	0.17	0.26		932.4	933
	5 Nov	1.30	3.5		123.9	128.7	0.72	0.11		923.8	925
	8 Nov	1.37	3.1		316.6	321.1	0.61	0.21	2.1	420.0	421
P3	9 Nov	0.62	7.3	78.7	365.5	373.4	0.26	0.30	3.0	808.5	809
	10 Nov	0.58	11.5	211.9	621.4	633.5	0.24	0.29	2.9	720.3	721
	12 Nov	0.27	7.5		802.4	810.2	0.27	0.14		995.5	996
	15 Nov	0.00	5.1	--	--	5.1	0.00	0.30			0.3
	16 Nov	0.40	3.3		594.3	598.0	0.45	0.25		289.7	290
	17 Nov	1.10	--	--	--	--	0.65	0.23	2.3	699.8	701
	19 Nov	0.96	0.5		732.8	734.3	0.38	0.35		659.3	660
	21 Nov	0.00	27.6			27.6	0.00	2.32	575.7		2.3
	22 Nov	0.60	16.2	933.2	454.8	471.5	0.45	0.58	568.5	821.0	822

Gray shaded results are considered anomalous

Table E6. Column 1 Concentration Calculations

	Date	Influent Air	Influent Water	Effluent Air	Effluent Water		
		C:NH3-N mg/L	NH3-N mg/L	NH3-N mg/L	NH3-N mg/L	NO2-N mg/L	NOX-N mg/L
P1	17 Oct	0.073	2.0E-02	1.5E-04	4.6		63.2
	20 Oct	0.075		1.2E-04	20.7		125.6
	22 Oct	0.050	1.0E-02	1.6E-04	0.9		171.2
	25 Oct	0.072	1.0E-01	1.6E-04	1.7	108	90.4
P2	26 Oct	0.204	0.0E+00	2.8E-04	7	180	220
	27 Oct	0.170	1.0E-02	5.2E-04	14	179	124.8
	29 Oct	0.101		1.5E-04	0.01		219.2
	1 Nov	0.157		1.5E-04	25.3		236.8
	3 Nov	0.156	0.0E+00	2.5E-04	3.4	95	340
	5 Nov	0.159		2.0E-04	44.9		465.6
	8 Nov	0.156	2.0E-01	2.1E-04	1.7	57	299.2
P3	9 Nov	0.090	1.0E-02	6.0E-05	0.5	67	348
	10 Nov	0.088		5.6E-05	1.5	64	255.2
	12 Nov	0.080	1.0E-02	2.1E-05	9.3		312.8
	16 Nov	0.081	1.0E-01	3.1E-05	0.09		272
	17 Nov	0.084	1.6E-01	8.6E-05	0.24	13	221.6
	19 Nov	0.072	0.0E+00	7.9E-05	0.13		211.2
	21 Nov	0.091		0.0E+00	6.24	187	
	22 Nov	0.090	1.2E-01	5.1E-05	0.91	241	360

Table E7. Column 2 Concentration Calculations

	Date	Influent Air	Influent Water				Effluent Air	Effluent Water			
		NH3-N mg/L	NH3-N mg/L	NO2-N mg/L	NOX-N mg/L	pH	NH3-N mg/L	NH3-N mg/L	NO2-N mg/L	NOX-N mg/L	pH
P1	17 Oct	1.5E-04	4.8		52	7.71	1.0E-04	0.01		125.6	8.1
	20 Oct	1.2E-04	--		98.4	7.74	1.1E-04	0.1		102.4	8.27
	22 Oct	1.6E-04	0.3		111.2		7.3E-05	0.1		68	8.43
	25 Oct	1.6E-04	--		--		1.2E-04	0.3		97.6	8.24
P2	26 Oct	2.8E-04	4.4		227.2		8.0E-05	0.1	47	192.8	8.74
	27 Oct	5.2E-04	7.6		0		6.7E-05	0.1	3	64	8.48
	29 Oct	1.5E-04	0.92		66.4	8.04	3.9E-04	0.88		208	8.37
	1 Nov	1.5E-04	1.1		305.6	8.43	1.2E-04	0.1		219.2	8.94
	3 Nov	2.5E-04	1	0	256	8.54	2.6E-05	0.1	0	360	8.72
	5 Nov	2.0E-04	1.3		45.6	8.55	1.1E-04	0.04		340	8.46
	8 Nov	2.1E-04	1.5		154.4	8.81	9.4E-05	0.1	1	204.8	8.89
P3	9 Nov	6.0E-05	2.4	26	120.8	8.58	2.5E-05	0.1	1	267.2	8.31
	10 Nov	5.6E-05	3.9	72	211.2	8.34	2.3E-05	0.1	1	244.8	8.74
	12 Nov	2.1E-05	2.2		236	8.02	2.1E-05	0.04		292.8	8.25
	15 Nov	--	1.7	--	--	8.70	--	0.1	--	--	9.22
	16 Nov	3.1E-05	1.06		190.4	8.43	3.5E-05	0.08		92.8	8.83
	17 Nov	8.6E-05	--	--	--	8.52	5.1E-05	0.1	1	299.2	8.87
	19 Nov	7.9E-05	0.15		231.2	8.78	3.1E-05	0.11		208	9.1
	21 Nov	0.0E+00	9.06			8.42	0.0E+00	0.76	189		8.81
	22 Nov	5.1E-05	6.43	371	180.8	8.17	3.8E-05	0.23	226	326.4	8.76

Gray shade

Table E8. System Operational Parameters for the Individual Periods and the Entire Study

Parameter	Ambient		System[1]				
	Temp °C	Humidity %	Temp °C	Humidity %	Air[2] L/min	NH_3-N mg/L	N Load[3,4] mg/d
Period 1							
Mean	**22.9**	**46**	**22.6**	**88**[5]	**4.5**	**0.07**	**496**
Std Deviation	1.0	15	1.1	13	0.3	0.012	96
High	24.4	78	24.4	93	5.1	0.075	681
Low	21.3	30	21.1	50	4.1	0.050	308
Period 2							
Mean	**24.1**	**39**	**23.4**	**85**[6]	**4.4**	**0.16**	**982**
Std Deviation	1.1	14	1.3	13	0.4	0.030	136
High	26.7	66	25.6	93	4.9	0.204	1355
Low	22.8	25	21.4	45	3.2	0.101	508
Period 3							
Mean	**23.2**	**43**	**22.9**	**91.3**	**8.5**	**0.08**	**1016**
Std Deviation	0.9	15	1.2	2	0.6	0.007	54
High	25.6	73	25.4	94	9.3	0.091	1067
Low	21.7	22	21.2	87	7.2[7]	0.072	112
Study							
Mean	**23.4**	**42**	**23.0**	**88.0**	[8]	[8]	[8]
Std Deviation	1.1	15	1.2	10			
High	25.6	78	25.6	94			
Low	21.7	22	21.1	45			

1. System measurements taken at Column 2 air effluent
2. Air flow is the average measurement over one day
3. Nitrogen mass loading based on volumetric change in ammonium hydroxide feed syringe, corresponds to calculated influent in Table F2
4. Transitient conditions are not included
5. Excluding the one low reading of 50%, the average humidity for the period is 91%
6. Excluding the one low reading of 45%, the average humidity for the period is 88%
7. System unable to sustain higher air flow
8. Operational conditions changed by design

Table E9. Column Operational Parameters for the Individual Periods and the Entire Study

Parameter	Column 1				Column 2			
	pH Inf[1]	pH Eff	Water[2] L/d	Headloss cm H_2O	pH Inf	pH Eff	Water[2] L/d	Headloss cm H_2O
Period 1								
Mean	**8.41**	**8.12**	**4.7**	**2.2**	**7.79**	**8.26**	**4.7**	**1.7**
Std Deviation	0.12	0.17	1.7	0.2	0.20	0.17	1.7	0.4
High	8.60	8.37	6.9	2.5	8.10	8.46	6.9	2.0
Low	8.27	7.78	2.9	1.9	7.63	7.98	2.9	1.5
Period 2								
Mean	**8.65**	**8.23**	**3.1**	**2.1**	**8.56**	**8.72**	**2.9**	**1.7**
Std Deviation	0.26	0.42	0.4	0.7	0.13	0.17	0.7	0.5
High	9.02	8.73	4.0	3.4	8.81	8.94	4.2	2.0
Low	8.06	7.19	2.2	1.3	8.34	8.37	2.1	1.2
Period 3								
Mean	**8.78**	**8.43**	**3.3**	**4.4**	**8.42**	**8.80**	**3.0**	**3.2**
Std Deviation	0.14	0.41	0.4	0.5	0.24	0.28	0.4	0.3
High	9.00	9.24	3.7	4.9	8.78	9.22	3.2	3.4
Low	7.61	7.71	2.7	3.2	8.02	8.25	2.3	2.5
Study								
Mean	**8.65**	**8.27**	**3.6[3]**	**2.9**	**8.29**	**8.61**	**2.9**	**2.2**
Std Deviation	0.23	0.38	1.1	1.2	0.37	0.31	0.5	0.8
High	9.02	9.24	6.9	4.9	8.81	9.22	6.9	3.4
Low	7.61	7.19	2.2	1.3	7.63	7.98	2.1	1.2

1. pH Meter, Orion Model 290A
2. Water flow is the average measurement over one day
3. Water flow was reduced from start-up conditions during Period 1;
   after adjustment the mean flow was 3.25 + 0.41 L/d

Table E10. NH_3-N Elimination Capacities for Columns 1 and 2, and the Entire System

Date	Column 1		Column 2		System	
	Loading Rate (kg N/m^3·d)	Elimination Capacity (kg N/m^3·d)	Loading Rate (kg N/m^3·d)	Elimination Capacity (kg N/m^3·d)	Loading Rate (kg N/m^3·d)	Elimination Capacity (kg N/m^3·d)
17 Oct	0.4273	0.3954	0.0319	0.0312	0.2135	0.2132
20 Oct	0.4694	0.3900	0.0794	0.0783	0.2346	0.2341
22 Oct	0.3040	0.3001	0.0039	0.0031	0.1519	0.1515
25 Oct	0.4739	0.4669	0.0070	0.0052	0.2368	0.2359
26 Oct	1.0034	0.9743	0.0292	0.0283	0.5015	0.5010
27 Oct	1.0633	1.0125	0.0508	0.0500	0.5314	0.5310
29 Oct	0.7103	0.7093	0.0010	0.0000	0.3550	0.3523
1 Nov	1.0081	0.9295	0.0786	0.0776	0.5038	0.5033
3 Nov	1.0233	1.0123	0.0110	0.0106	0.5114	0.5112
5 Nov	1.0224	0.8800	0.1424	0.1415	0.5109	0.5105
8 Nov	1.0008	0.9949	0.0059	0.0051	0.5001	0.4997
9 Nov	0.9827	0.9806	0.0020	0.0015	0.4911	0.4908
10 Nov	0.9786	0.9727	0.0059	0.0053	0.4890	0.4888
12 Nov	1.0317	1.0002	0.0315	0.0311	0.5156	0.5154
16 Nov	1.0052	1.0045	0.0007	0.0004	0.5024	0.5022
17 Nov	1.0497	1.0478	0.0019	0.0012	0.5246	0.5242
19 Nov	0.8637	0.8623	0.0014	0.0005	0.4316	0.4312
21 Nov	1.0536	1.0337	0.0199	0.0192	0.5265	0.5262
22 Nov	1.0493	1.0461	0.0032	0.0009	0.5244	0.5233

Table E11. Nitrogen Mass Balance Data

	Date	Influent C1 mg/d	Effluent C1 mg/d	Effluent C2 mg/d	Std Dev[1]	% Dev[2]
P1	17 Oct	433	463	856	236	40
	20 Oct	476	564	395	84	18
	22 Oct	308	557	220	175	48
	25 Oct	480	392	349	67	16
P2	26 Oct	1016	901	765	126	14
	27 Oct	1077	666	221[3]	290	33
	29 Oct	720	710	678	22	3
	1 Nov	1021	816	630	196	24
	3 Nov	1037	962	933	53	5
	5 Nov	1036	1626	925	377	32
	8 Nov	1014	824	421	303	40
P3	9 Nov	995	989	809	106	11
	10 Nov	991	916	721	140	16
	12 Nov	1045	1095	996	50	5
	16 Nov	1018	963	290	405	54
	17 Nov	1063	768	701	193	23
	19 Nov	875	717	660	111	15
	22 Nov	1067	1045	822	136	14
Study Averages					171	23

1. Standard Deviation calculated for each set of daily samples
2. % Dev = Std Dev / Average N Loading for each day * 100
3. Shaded resions identify erroneous results and were not included in subsequent calculations

Table E12. Summarized Ammonia (NH_3-N) Removal

	Date	mg/d	%
P1	17 Oct	432	99.83
	20 Oct	474	99.77
	22 Oct	307	99.74
	25 Oct	478	99.61
	Mean	**423**	**99.74**
P2	26 Oct	1016	99.91
	27 Oct	1076	99.93
	29 Oct	714	99.25
	1 Nov	1020	99.90
	3 Nov	1036	99.96
	5 Nov	1035	99.92
	8 Nov	1013	99.92
	Mean	**987**	**99.83**
P3	9 Nov	995	99.94
	10 Nov	991	99.95
	12 Nov	1045	99.96
	16 Nov	1018	99.97
	17 Nov	1063	99.93
	19 Nov	874	99.90
	22 Nov	1067	99.93
	Mean	**1007**	**99.94**

Influent NH3-N (Air & Water)
- Effluent NH3-N (Air & Water)

Ammonia Removed (mg/d)

$$\frac{\text{Ammonia Removed (mg/d)}}{\text{Influent NH3-N (mg/d)}} * 100 = \% \text{ Removed}$$